The Analysis of Taupo Pumice as an Effective Partial Cement Replacement in Concrete

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Frontispiece

“Man's mind, once stretched by a new idea, never regains its original dimensions.”

Oliver Wendell Holmes

Abstract

Concrete is an integral material in modern infrastructural requirements worldwide. The production of Portland cement is however expensive, energy intensive, and results in globally significant greenhouse gas emissions. Natural pozzolans such as pumice can be used as a partial replacement for Portland cement in concrete, which can reduce production costs and greenhouse gas emissions, and improve concrete performance.

A fluvial pumice deposit which may be suited for use as a natural pozzolan has been identified on the floodplains of the Waikato River. A sample was milled in Germany, and returned to New Zealand in two subsamples. These were tested in concrete, with tests divided into four rounds. The first two rounds established baseline concrete strengths at water/binder (w/b) ratios of 0.6 and 0.5, with pumice replacing cement at 5, 10, 15 and 30%. Round Three assessed the use of high pH mix water (pH=12.9), and Round Four assessed the use of a polycarboxylate superplasticiser, both with 10% pumice.

Pumice is known to retard early concrete strength, however through optimisation of mix design, improvements in concrete strength and durability can be made. Indeed, all 28 day concrete strengths in this research were below Ultracem, however half of these achieved or exceeded Ultracem strengths at 91 days. The use of superplasticiser achieved the best 28 day concrete strengths, and dosage optimisation is expected to yield further improvements.

Concrete durability was tested at w/b=0.5, with 10% and 30% pumice. After prolonged curing (231 days), composite concrete showed substantial improvements in electrical resistivity and resistance to chloride attack, most notably with 30% pumice. Concrete porosity was essentially unaffected.

This pumice has shown significant promise as a partial cement replacement. Further mix optimisation is likely to yield greater improvements in concrete strength and durability, and will provide a more economically and environmentally sustainable product for the New Zealand concrete market.

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Table of Abbreviations

AR ..... Alumina Ratio
AS ..... Australian Standard
ASR ..... Alkali Silica Reaction
ASTM ..... American Society for Testing Materials
CKD ..... Cement Kiln Dust
GB ..... General Purpose Blended
GGBS ..... Ground Granulated Blast Furnace Slag
GP ..... General Purpose
GPS ..... Global Positioning System
HGL ..... High Grade Limestone
IRL ..... Industrial Research Limited
LOI ..... Loss on Ignition
LSF ..... Lime Saturation Factor
NaEq ..... Sodium Equivalent
NZS ..... New Zealand Standard
OPC ..... Ordinary Portland Cement
PSD ..... Particle Size Distribution
SCM ..... Supplementary Cementitious Material
SF ..... Silica Fume
PFA ..... Pulverised Fuel Ash
SEM ..... Scanning Electron Microscope
SP ..... Superplasticiser
SR ..... Silica Ratio
SSA ..... Specific Surface Area
SSD ..... Saturated Surface Dry
TGA ..... Thermogravimetric Analysis
TOC ..... Total Organic Carbon
TVZ ..... Taupo Volcanic Zone
w/b ..... Water/Binder (ratio)
w/c ..... Water/Cement (ratio)

WR ..... Water Reducer

XRD ..... X-Ray Diffraction

XRF ..... X-Ray Fluorescence

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Effects of Christchurch Earthquakes

On February 22nd 2011, Christchurch was struck by a devastating 6.3 magnitude earthquake, and several thousand subsequent aftershocks. This resulted in a number of changes to this thesis, and some of the methods used.

Concrete testing was initially scheduled to begin in February 2011 at the University of Canterbury Civil Engineering concrete laboratory. With the closure of the University for several weeks, and its staggered re-opening, the decision was made to transfer most concrete testing to the Holcim concrete laboratory in Westport.

This laboratory was chosen for several reasons. Firstly, with large aftershocks expected for months after the main event, the risk of laboratory closure during the year could not be ruled out. This proved important when the University was again briefly closed in June and December due to large aftershocks.

Secondly, familiarity with testing procedures and protocol in the Holcim laboratory provided an opportunity to improve testing efficiency, and variations in methods and equipment could be minimised. Good relationships with laboratory staff meant that once cylinders were cast, they could be broken at appropriate intervals by suitably qualified personnel. It also meant that additional guidance and support was provided, and allowed knowledge of previous pumice-concrete testing to be readily utilised.

The only other major change influenced by the earthquakes was the type of cement used, where testing delays resulted in a more modern product being available for the second and subsequent rounds. This is explored in more detail in Section 5.5.

Nomenclature

Admixture*	A material other than water, aggregate and cementitious materials, added to concrete to achieve a desired performance modification.
Air entrainment	The intentional creation of microscopic air bubbles distributed throughout a concrete paste.
Binder	Any cementitious material, including Portland cement and pozzolans.
Blended concrete	A concrete in which cement has been partially substituted with a pozzolan.
Clinker factor	Proportion of clinker per unit of cement.
Cement*	Portland cement complying with NZS 3122 or NZS 3123.
Concrete*	A mixture consisting predominantly of cement, water and aggregate.
Curing	The process by which the moisture content and temperature of concrete are maintained to facilitate cement hydration.
Fly ash*	Material extracted from the flue gases of a coal fired boiler which complies with AS 3582.1.
Mortar*	A mixture consisting predominantly of cement, water and sand.
Oversubstitution	Where in a concrete mix, pozzolan is added to replace a portion of both cement and sand, effectively increasing total binder content.
Paste	A mixture of cement and water in its fresh, unhardened, plastic state.
Pozzolan*	A siliceous material which when finely ground and in the presence of water reacts with calcium hydroxide, forming hydration products similar to those of Portland Cement. Such pozzolans shall comply with NZS 3123.
Pumice	A deposit dominantly consisting of vesicular volcanic glass of rhyolitic composition.
Reference cement	Ultracem cement used as a benchmark against which other tests are compared.
Sand*	Aggregate passing a 4.75mm sieve.
Slag	Calcium silicates and aluminosilicates produced simultaneously with iron in a blast furnace. Granulated iron blast-furnace slag shall comply with AS 3582.2.
Slump*	The amount by which a standard amount of concrete subsides upon removal from a slump cone. Conducted in accordance with NZS 3112.
Ultracem	Holcim General Purpose (GP) cement conforming with NZS 3122.
Water reducer	An admixture which disperses cement particles, increasing concrete fluidity. Its addition will reduce the water required to achieve a given workability.
Workability*	A measure of the ease in which concrete paste can be mixed, placed, compacted and finished.

* Definitions taken from appropriate New Zealand Standards

Chapter 1 Introduction

1.1 Sustainable Production of Portland Cement

Cement and concrete are integral in meeting modern society's infrastructural needs, therefore increasing the sustainability of cement production is of mounting urgency and consequence. Portland cement is produced by burning a blend of calcium carbonate (eg. limestone or chalk) and aluminosilicate (eg. clay or shale) at high temperatures (approximately 1450°C) to form clinker. This is then interground with gypsum, and additional limestone (Bye, 1999).

The terms 'cement' and 'concrete' are used somewhat interchangeably in general conversation. For purposes of this investigation, the term 'concrete' shall refer only to a combination of water, binder, aggregate, and admixtures, either in its fresh (paste) or hardened state. The term 'cement' shall refer only to Portland cement, unless otherwise specified.

The cement and concrete industry is subject to a number of challenges in modern markets. In the production of clinker, both the combustion of fossil fuels (coal and oil) and decarbonation of limestone release significant quantities of carbon dioxide (CO_2). The amount of CO_2 emitted varies between manufacturing plants and their respective processes, but can range from 0.6-1 tonnes of CO_2 per tonne of clinker (Yousni, et al., 2011). Consequently, primary issues facing the industry on a global scale include vast thermal energy consumption and CO_2 emissions. The Portland cement manufacturing process is energy intensive, with energy accounting for 30-40% of production costs. Across the industry, this equates to an estimated 2% of global energy consumption, and almost 5% of industrial energy consumption (Szabo, et al., 2006).

China is the world's largest cement producing and consuming nation. In 2008, Chinese cement production totalled 1.39 billion tonnes, accounting for approximately 50% of global production (Lei et al., 2011). Interestingly, in their study of global cement production and consumption, Szabó et al., (2006) identified the OECD Pacific (Australia, Japan and New

Zealand) as the region with the highest per capita cement consumption, totalling 568kg of cement per person in 1997 (Figure 1.1). This is in contrast with more recent national data, indicating New Zealand's 2006 cement consumption was approximately 321kg per person[1]. In reality, per capita consumption will have likely decreased further due to the influences of economic recession and global financial crisis.

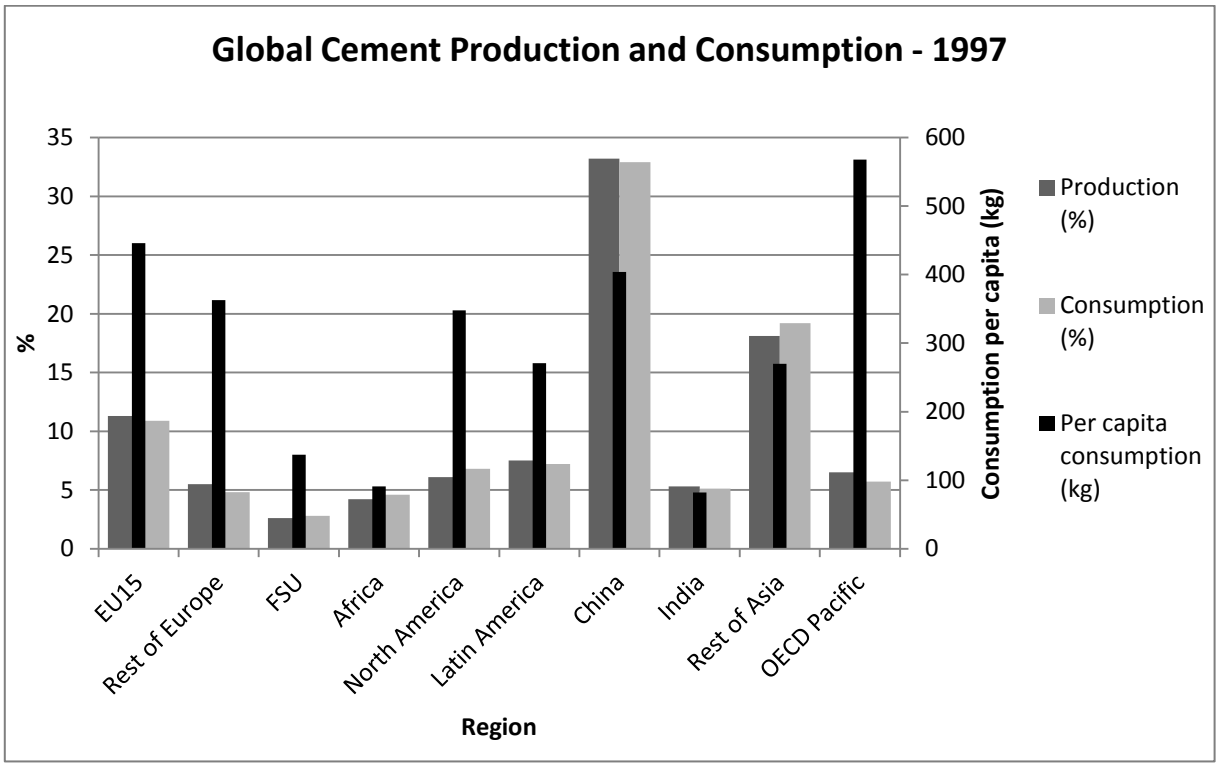


Figure 1.1: Global cement production and consumption

EU15 - Austria, Belgium, Denmark, Finland, France, Germany, Greece, Ireland, Italy, Luxembourg, the Netherlands, Portugal, Spain, Sweden and the United Kingdom

FSU – Former Soviet Union

International legislation and public attitude continually advance toward improving industrial efficiency and reducing its environmental impact. Improving the sustainability of cement production is therefore a principal focus throughout this investigation. Sustainable development is defined by the World Business Council for Sustainable Development (WBCSD) as "*forms of progress that meet the needs of the present without compromising the*

[1] This is based on New Zealand's 2006 estimated maximum cement producing capacity (1.35 million tonnes), a population of 4.2 million people, and assumes no imports (New Zealand Institute of Economic Research, 2008; Statistics New Zealand, 2011).

ability of future generations to meet their needs" (Damtoft, et al., 2008). The WBCSD has identified four foci where CO_2 emissions can be reduced in the cement industry worldwide. These are as follows (Lei, et al., 2011):

- Improving thermal and electric efficiency
- Utilising alternative fuels
- Clinker substitution
- Carbon capture and storage

The former three initiatives are consistent with the New Zealand cement industry's current emissions response strategy, while the latter may play a more important role in the future. Although New Zealand emits only approximately 0.2% of total global greenhouse gases, significant efforts are still being undertaken to reduce emissions and address potential climate change (Gray, et al., 2002).

1.1.1 Sustainable Cement Production in New Zealand

The New Zealand construction industry presents an interesting market situation with unique contests and challenges. New Zealand Portland cement is produced in two locations, namely Westport (Holcim NZ Ltd) and Whangarei (Golden Bay Cement). Due to market influences, New Zealand cement is produced with mortar strengths well in excess of minimum standards specified by New Zealand Standard (NZS) 3122:2009[2]. Consequently, when trialling new materials and methods, it is necessary to target concrete and mortar strengths which conform not only with NZS 3122, but the expectations of the New Zealand market. A selection of Holcim Ultracem mortar strengths are provided in Figure 1.2, and Ultracem concrete strengths are shown in Figure 1.3[3]. Each are the results of testing conducted in Holcim's Westport laboratory.

Numerous incentives contribute to the addition of supplementary cementitious materials (SCM's) in the New Zealand concrete market. Of primary significance is the global initiative to reduce energy consumption and greenhouse gas emissions, and associated fiscal

[2] Specification for Portland and blended cements (General and special purpose)

[3] 30MPa Ultracem, water/binder ratio = 0.6.

implications. These are accompanied by increasing fuel costs, excise taxes, public sensitivity to climate change, and the implicit need to universally revolutionise consumptive patterns.

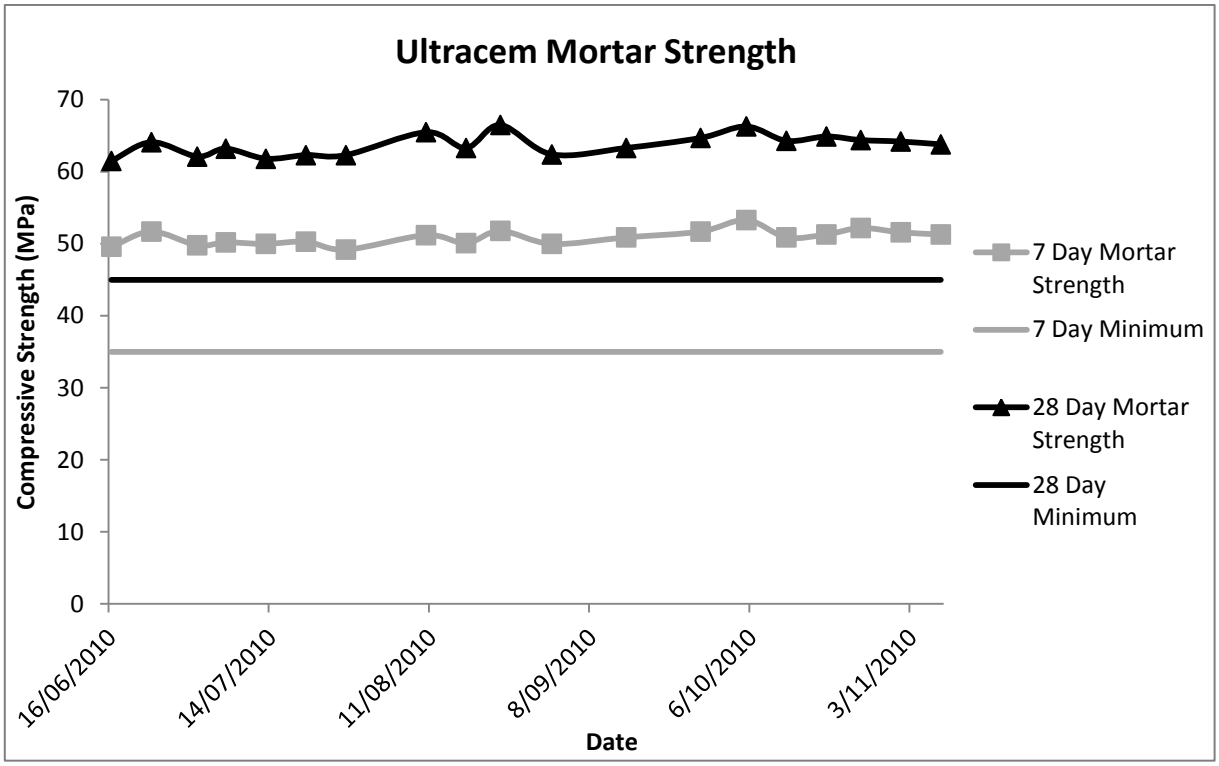


Figure 1.2: Ultracem mortar strength

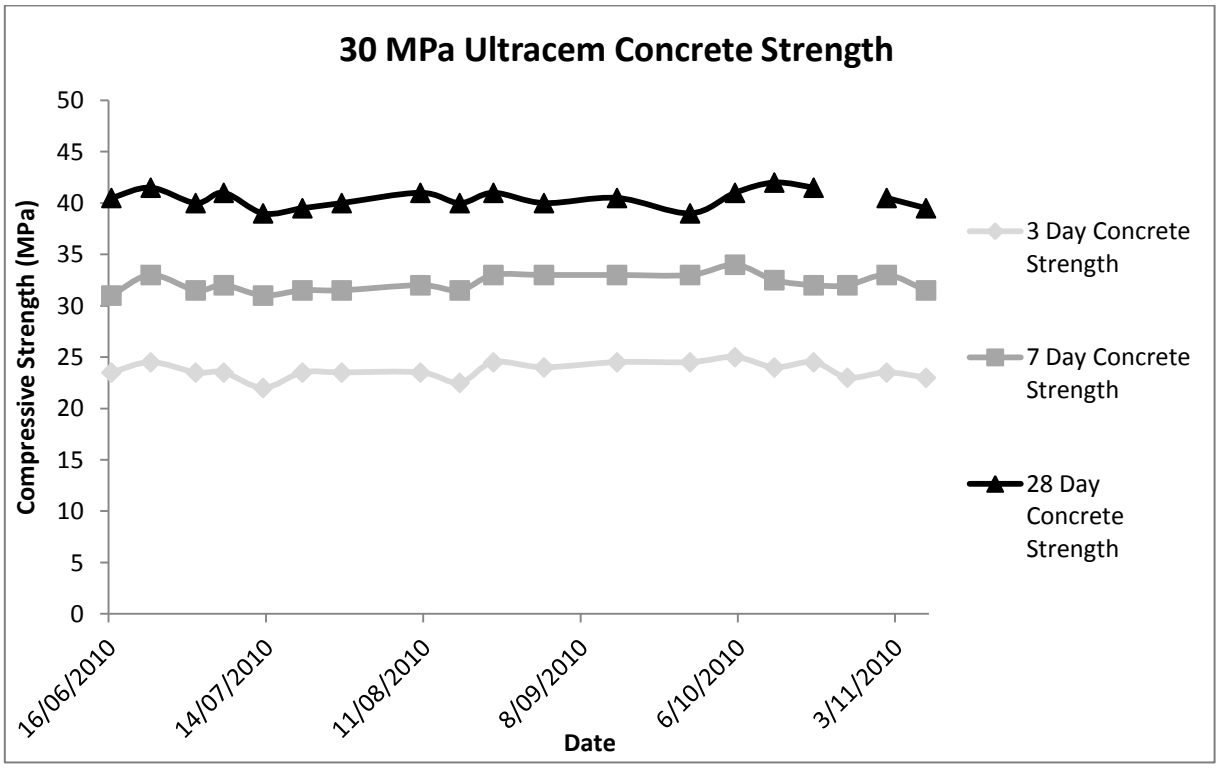


Figure 1.3: Ultracem concrete strength

Both the New Zealand and global cement industries identify reducing clinker factor[4] as presenting the greatest immediate potential to reduce greenhouse gas emissions. Reductions can be achieved using SCM's such as limestone, fly ash, blast furnace slag or natural pozzolans as partial cement replacements (Gray, et al., 2002).

Greenhouse gas emissions associated with the preparation of raw pumice (primarily drying, milling and transport) are considerably less than those associated with clinker manufacture. Therefore, if significant pumice substitution is successful, an appreciable greenhouse gas reduction can also be achieved. New Zealand is fortunate to possess significant volcanic deposits. Some of these are suited for utilisation as natural pozzolans, and have the potential to significantly reduce the clinker factor of New Zealand cements. The challenge in this research is to prove the viability of Taupo pumice from Rangiriri, Waikato, as a partial cement replacement, whilst maintaining or improving concrete performance.

1.1.2 Challenges in the New Zealand Market

Incorporating new materials and techniques into the New Zealand cement and concrete market is not without challenges. The New Zealand construction industry has previously demonstrated a reluctance to accept unfamiliar products. Therefore, key stakeholders must be educated and wholly satisfied as to the quality of any new cement before it will gain commercial acceptance. To fully utilise natural resources and minimize environmental impact, it is necessary to not only improve the efficiency by which cement is produced, but the efficiency in which it is consumed. Pumice is not an unproved concrete additive, and has in fact been used as a lightweight concrete aggregate for over 2000 years. In more modern times, pumice aggregates have been combined with Portland cement and water to produce thermal and sound insulating, fire-resistant, lightweight concrete. These have been used in a variety of applications, including roof decks, lightweight floors, prefabricated and in situ masonry (Gunduz, 2008).

The difficulties in achieving both performance and market acceptance were illustrated in a recent endeavour involving Holcim (NZ), where the addition of mineral limestone in General

[4] The proportion of clinker per unit of cement.

Purpose (GP) cement was increased from 5% to 10%. Facilitating this involved amending NZS 3122, as well as demonstrating to key industry stakeholders that the new product met all performance expectations. Many aspects of this are relevant to the incorporation of pumice into GP or General Purpose Blended (GB) cements throughout New Zealand. NZS 3122 has now been successfully amended, and production of 10% limestone GP cement commenced in April 2011. As such, this research will be conducted using the most modern cement type available.

1.1.3 Natural Pozzolans in Construction

Natural pozzolans have been combined with lime in construction materials since ancient times. The mortar used in historically significant structures such as the Pantheon, Colosseum, Tournai Cathedral and Domitilla Catacombs all contain natural pozzolans (Ozkaya & Boke, 2009). Modern cements and concretes utilise natural pozzolans on the basis that they can enhance certain properties, including strength, permeability, sulphate resistance, and alkali-silica reaction (Turanli, et al., 2004). Pozzolans also have the potential to reduce production costs through reduced clinker factor and greenhouse gas emissions.

Pozzolans include those inorganic materials, either natural or artificial, which harden in water when mixed with calcium hydroxide (lime). Pozzolanic cements have been developed to utilise both industrial and natural materials. These include silica fume, fly ash, blast furnace slag, pyroclastic rocks, diatomaceous earth and agricultural by-products (Hewlett, 1998). Natural pozzolans can be further defined as raw or calcined natural materials which have pozzolanic properties, such as volcanic ash, opaline chert, shales and tuff (Turanli, et al., 2004). The pozzolanic reaction is essentially between reactive, non-crystalline or amorphous silica and lime (South, 2009), and is further explained in Section 2.5.

Natural pozzolans commonly contain carbonate, clay and zeolite group minerals. Zeolitization is the process where the glassy structure of a natural pozzolan is transformed into zeolite group minerals, which can lose their water content when heated (Cavdar & Yetgin, 2007). Zeolite minerals have a cage-like aluminosilicate structure, with a high internal and external surface area. Zeolite tuffs (activated with lime) have also been widely used in the construction of ancient structures (Perraki, et al., 2010).

1.2 Thesis Scope

The cement industry is investigating methods by which cement clinker factor can be reduced, improving production efficiency, concrete performance, and reducing environmental impact. Previous investigations have identified a pumice resource at Rangiriri, Waikato, as having the potential for development as a commercial reserve. This thesis undertakes an investigation of Taupo pumice from Rangiriri as an effective partial cement replacement in GB concrete. This includes extensive concrete strength and durability analyses at various pumice-cement blends, and a range of chemical and mineralogical tests. The influence of particle fineness and the application of concrete admixtures are considered, as are the mechanisms by which natural pozzolans behave in cement. Where appropriate, results are compared with previous investigation of similar pumice from Horotiu.

1.2.1 Concrete Testing

Once adequately milled pumice has been obtained, a range of concrete tests will be conducted using pumice as a partial cement replacement. Pumice replaced cement at 5, 10, 15 and 30% in a series of concrete batches, identifying changes in workability, air entrainment, compressive strength and durability. All tests are benchmarked using an appropriate Ultracem reference concrete.

Testing is divided into four stages, identified as Rounds One, Two, Three and Four. Outcomes of a given round influence the mix design in the subsequent round(s). Additionally, the use of a scanning electron microscope (SEM), thermo-gravimetric analysis (TGA), x-ray fluorescence (XRF) and x-ray diffraction (XRD) are utilised to further establish the chemical and physical nature of the milled pumice, and its interactions in the hydration process.

1.2.2 Thesis Outline

This research addresses several aspects of natural pozzolans and how they interact with cement and concrete. Chapter 2 investigates the chemical and physical properties related to cement hydration, including a summary of various supplementary cementitious materials (SCM's), and how they interact in the hydration process. Chapter 3 investigates natural

pozzolans in more detail, and Chapter 4 assesses blended concrete durability. Chapter 5 presents the methods used in this thesis, including milling and concrete preparation. Mix designs are provided in Chapter 6, and results and discussion in Chapter 7. Chapter 8 presents conclusions, and finally, recommendations are provided in Chapter 9.

Chapter 2 Cement Hydration

In order to understand the chemistry and behaviour of natural pozzolans in cement and concrete, it is necessary understand fundamental cement chemistry, and the associated hydration reactions. Understanding the kinetic mechanisms of cement hydration is of both practical and academic interest, especially as more complex designs incorporate a wide variety of admixtures. A more complete knowledge of basic hydration mechanisms provides a more rational base for the incorporation of supplementary cementitious materials (Bullard, et al., 2010).

Portland cement clinker consists of four major phases of strength forming compounds. Each compound reacts with water to form different hydration products, gradually filling the voids between aggregate particles, forming a continuous cementitious matrix. Formulae are commonly written as combinations of oxides using cement chemists notation, presented in Table 2.1 (Taylor, 1997), and Table 2.2.

Table 2.1: Cement chemists notation

Notation	Formula
C	CaO
S	SiO_2
A	Al_2O_3
F	Fe_2O_3
M	MgO
K	K_2O
$\bar{S}$	SO_3
N	Na_2O
T	TiO_2
P	P_2O_5
H	H_2O
$\bar{C}$	CO_2

Table 2.2: Summary of strength forming compounds in OPC

Compound	Name	Formula	Notation	Weight Fraction (%)
Tricalcium silicate	Alite	Ca_3SiO_5	C_3S	50-70
Dicalcium silicate	Belite	Ca_2SiO_4	C_2S	15-30
Tricalcium aluminate	Aluminate	$Ca_3Al_2O_6$	C_3A	5-10
Tricalcium aluminoferrite	Ferrite	$Ca_4Al_2Fe_2O_{10}$	C_4AF	5-15
				Adapted from Young et al., 1998

2.1 Water/Cement Ratio

One of the most fundamental properties in determining concrete strength is the water/cement (w/c) ratio. As this research is based upon the partial replacement of cement with a natural pozzolan, the term water/binder (w/b) ratio is used to reflect the composite nature of the total binder.

Concrete compressive strength is a function of the closeness of cement particles as well as cement content (Aitcin, 2000). The w/c ratio is inversely proportional to concrete strength, where lower w/c ratios result in higher strength concretes. This ratio heavily controls paste porosity, and is a key parameter in determining concrete quality (Kharita, et al., 2010).

2.2 Heat of Hydration

The hydration of Portland cement is associated with the liberation of heat, and is therefore a dominantly exothermic process (with a minor intermediate endothermic stage). Cements containing small amounts of K^+ in the form of potassium sulphate may display a distinct initial endothermic peak (Figure 2.1) [1]. This occurs immediately after mixing, and is due to the dissolution of potassium sulphate into mix water.

This is followed by an intense exothermic stage [2] within a few minutes, due to the rapid hydration of alite (see Section 2.3) and aluminate (see Section 2.4), as well as possible contributions from the hydration of calcium sulphate hemihydrate to dihydrate. A distinctive minimum is typically observed due to a dormant period in which the overall hydration rate is slowed [3], followed by an exothermic peak [4] and the formation of C-S-H. Beyond this, heat liberation abates to very low values within a few days (Hewlett, 1998).

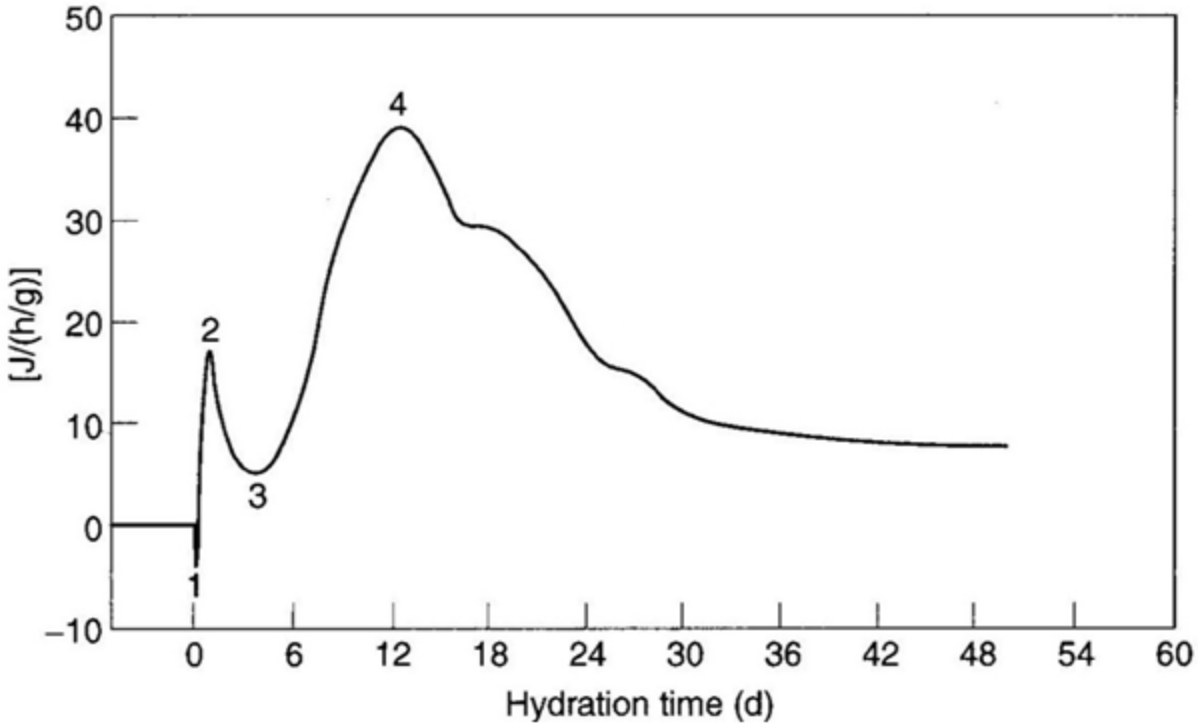


Figure 2.1: Hydration heat evolution of Ordinary Portland Cement.
1: K_2SO_4 dissolution; 2: early stage reaction; 3: dormant period; 4: middle-stage reaction (C-S-H formation) (Hewlett, 1998)

2.3 Hydration of Alite and Belite

The primary strength forming compound created in the clinker phase is alite, which constitutes 50-70% of clinker composition. Alite is a tricalcium silicate (Ca_3SiO_2 or C_3S), and is the most instrumental strength forming compound in the first 28 days of curing. Pure C_3S contains 73.7% CaO, and 26.3% SiO_2, with clinker alites typically containing 3-4% substituent oxides (Taylor, 1997).

The initial reaction occurs between C_3S and water immediately upon wetting, and is characterised by a large exothermal signature in isothermal calorimetry. Heat is released both by wetting the cement powder and from the dissolution of C_3S (Bullard, et al., 2010). The hydration of alite is complex, and not fully understood. At ambient temperatures, hydration products consist of an amorphous calcium silicate hydrate phase with a CaO/SiO_2 ratio <3.0 (C-S-H), and calcium hydroxide. The following reaction is observed (Hewlett, 1998):

$3CaO.SiO_2 + (3+m-n)\ H_2O \rightarrow nCaO.SiO_2.mH_2O + (3-n)\ Ca(OH)_2$

C_3S can exist in several polymorphs (Figure 2.2), dependent on the amount and composition of substituent ions. At ambient temperatures, only Type 1 (T_1) C_3S (pure C_3S) is formed, however the presence of other cations such as magnesium, aluminium and other transition metals may stabilise polymorphs, replacing either Ca^{2+} or Si^{4+} depending on the size and charge of the ion. Ordinary Portland Cement (OPC) may contain any combination of triclinic, monoclinic and trigonal C_3S; however the monoclinic form tends to dominate (Hewlett, 1998; Stewart & Bailey, 1983).

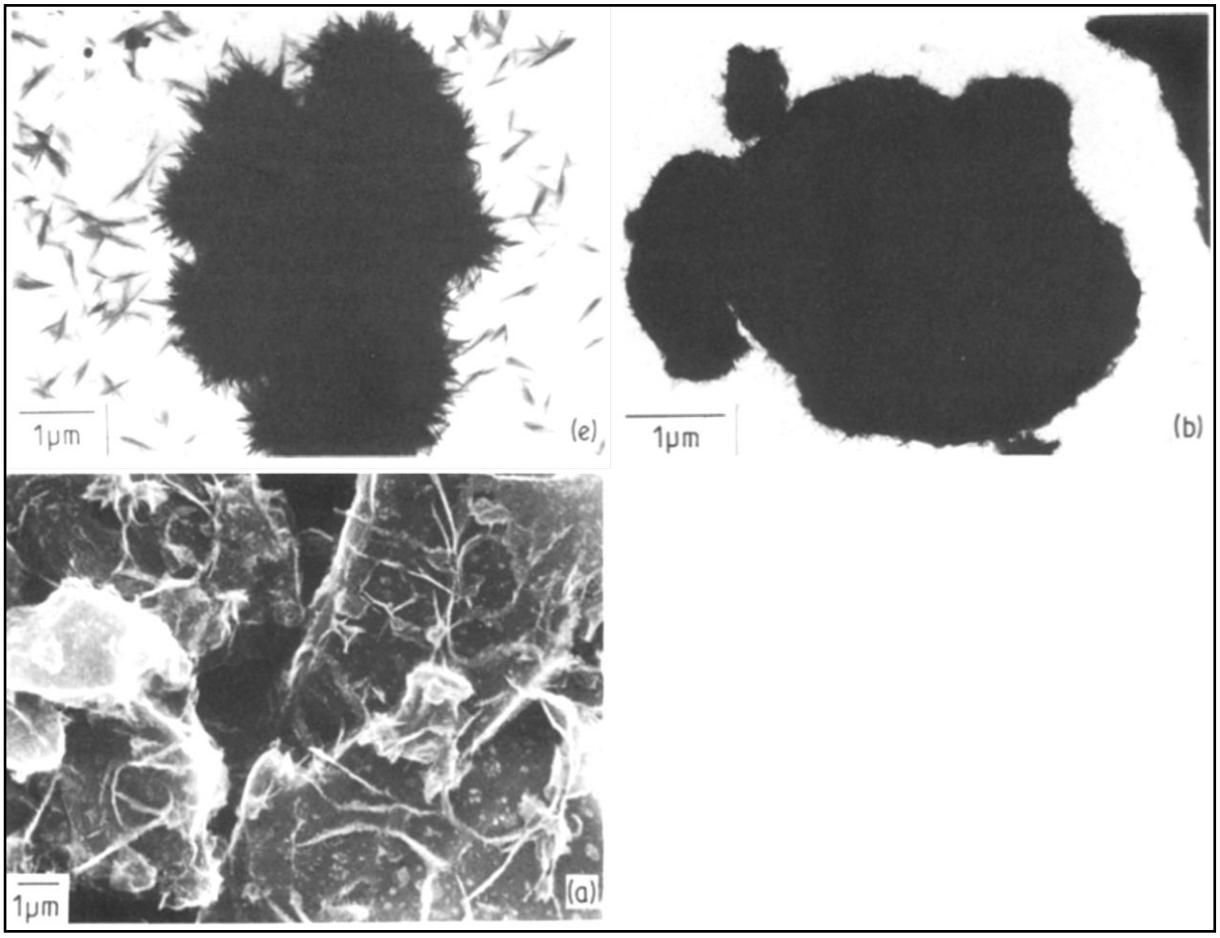


Figure 2.2: SEM images of C_3S polymorphs at 24 hours hydration
Triclinic (top left), trigonal (top right), monoclinic (bottom left) (Stewart & Bailey, 1983)

Belite (Ca_2SiO_4 or C_2S) is the second most important strength forming compound in Portland cement, constituting 15-30% of clinker composition. Pure C_2S contains 34.9% SiO_2 and 65.1%

CaO. Clinker belites normally contain 4-6% substituent oxides (dominantly Al_2O_3 and Fe_2O_3) (Taylor, 1997). C_2S reacts slowly with water, contributing little to concrete or mortar strength in the first 28 days, but contributing substantially as it ages.

C_2S exists in five polymorphs at regular pressures, and as for C_3S, higher temperature polymorphs cannot be retained at regular cooling temperatures unless stabilised by foreign ions (Taylor 1997). The most common polymorph is β-C_2S, which can be stabilised at all temperatures, including ambient temperatures in the presence of certain substituent ions. β-C_2S is often contaminated with γ-C_2S, which is also thermodynamically stable at ambient temperatures (Hewlett, 1998).

Alite and belite are formed above 800ºC, where C_3S is preferentially formed by elevating kiln temperature and increasing the addition of burned lime. A cement kiln at the Westport Cement Works is shown in Figure 2.3. C_3S is critical in short term strength development (days to months), whereas C_2S is more important in long term (years) performance (Ylmen, et al., 2009). Both calcium silicate phases give similar hydration products; an amorphous calcium silicate gel (C-S-H), and crystalline calcium hydroxides. The two phases do however hydrate at significantly different rates, especially during the first 24 hours of curing (Stewart & Bailey, 1983).

The term C-S-H is used to represent amorphous or nearly amorphous calcium silicate hydration products with the general formula $CaO_x{\cdot}SiO_2{\cdot}H_2O_y$ where both x and y can vary widely (Hewlett, 1998). The gel is actually composed of a less polymerised metastable precursor of crystalline tobermonite or jennite, which tends to convert to a more polymerised form with elevated temperatures and time (Bruno, 2007).

Figure 2.3: Cement kiln – Holcim NZ Westport Cement Works

2.4 Hydration of Aluminate and Ferrite

Aluminate ($Ca_3Al_2O_6$ or C_3A) comprises 5-10% of clinker composition, and reacts vigorously with water, rapidly forming hydration products. This phase quickly reduces workability, and instruments early concrete set. The hydration of C_3A is therefore controlled by the addition of gypsum ($CaSO_4.2H_2O$ or $C\bar{S}$), which reacts with C_3A to form ettringite. Ettringite is an intermediate mineral which encases C_3A particles, retarding the reaction (Young, et al., 1998). C_3A exists in cubic, orthorhombic and monoclinic polymorphs, again dependent on the presence and composition of foreign ions (especially Na^+). Clinker C_3A exists almost exclusively in the cubic form (Hewlett, 1998; Lee et al., 1982)

In the absence of gypsum, C_3A hydrates to form hexagonal crystals (C_2AH_8 and C_4AH_{19}), which eventually convert to cubic C_3AH_6, the only thermodynamically stable C_3A polymorph at ambient temperatures. In the presence of gypsum however, the amount of C_3A hydrated in the early stages of curing is significantly reduced, and ettringite ($C_6A\bar{S}_3H_{32}$) and

monosulphate ($C_4A\bar{S}H_{12}$ or C_4AH_{19}) are formed instead. These reactions are accompanied by significant heat release (Figure 2.4) (Hewlett, 1998).

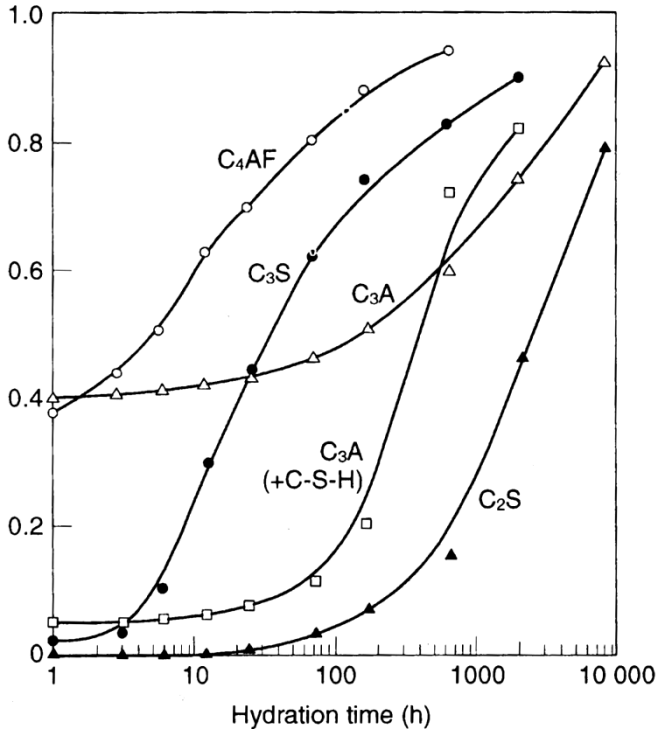


Figure 2.4: Hydration kinetics of pure clinker at ambient temperatures
(Hewlett, 1998)

The method by which gypsum retards the hydration of C_3A is debatable, with two main theories. The first, as previously mentioned, is where a protective layer of ettringite (or another mineral) is formed around the aluminate particles, forming an impervious layer and preventing rapid hydration. The second is that retardation is due to the formation of positively charged C_3A particles by adsorption of calcium, or the adsorption of sulphate ions, reducing sites of active dissolution. Under this theory, ettringite has no relationship with the retardation of C_3A hydration (Plowman & Cabrera, 1984).

Ferrite ($Ca_4Al_2Fe_2O_{10}$ or C_4AF) forms 5-15% of clinker composition, and reacts similarly to C_3A. Ferrite hydration is also retarded in the presence of gypsum (Taylor, 1997). It was long thought that the C_4AF phase did not contribute to concrete or mortar strength, and this is to an extent still uncertain. However, with the inclusion of blast furnace slag in many cement

blends worldwide, cements with up to 16.7% C_4AF have been successfully used in oil well and geothermal systems (Fukuhara, et al., 1981).

C_3A and C_4AF phases also result in the formation of AFt (dominantly ettringite) and AFm (dominantly monosulphate) phases, each of which are regular constituents of hydrated cement pastes. The AFt phase is formed at the beginning of the hydration process, and is instrumental in preventing early concrete set. However, it is also believed to be responsible for concrete expansion in cements with excessive SO_3, or when concrete structures are exposed to sulphate bearing groundwater. The AFm phase is formed from AFt with additional C_3A, C_4AF, or free calcium sulphate. Both tend to undergo further changes during the course of cement hydration to eventually form hydrogarnet phases (Odler & Abrul-Maula, 1984; Taylor, 1997).

Pozzolanic activity in the early ages of the lime-pozzolan reaction is largely dependent on pozzolan surface area, where longer term activity is thought to depend more heavily on the chemical and mineralogical composition of the pozzolan itself. Ca-Al hydrates and amorphous C-S-H gel are generally formed after one day of curing. Aluminate hydrates form later, however their rate of formation is dependent on the pozzolan aluminium content and solubility (South, 2009).

2.5 Cement Hydration with Pozzolanic Additives

The primary reaction in any pozzolanic system involves OH^- ions attacking the SiO_2 or Al_2O_3-SiO_2 pozzolan framework. OH^- ions combine with pozzolan network forming atoms such as silicon, breaking bonds between these and oxygen. Consequently, silicate (or other) oxy anions are released from the framework, and may remain in situ or pass into solution. The charges of those which remain are balanced by H^+ and metal cations. Reaction products include a C-S-H gel with a low Ca/Si ratio, and the formation of strätlingite, hydrogarnet, or both (Taylor, 1997).

The addition of pozzolans (both natural and industrial by-products) affects many aspects of cement hydration, including reaction kinetics, formation of calcium hydroxide (portlandite),

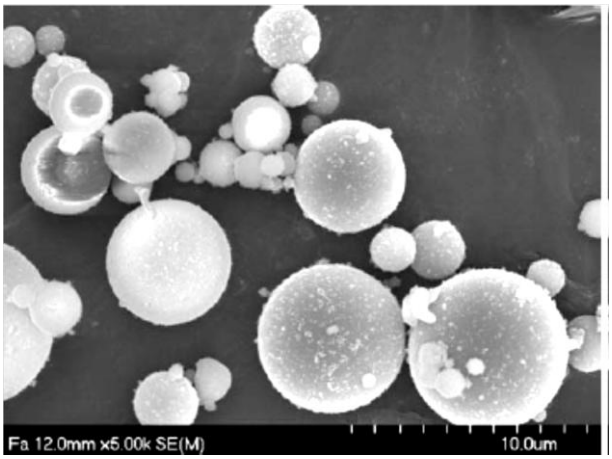
and hydrate composition. The addition of certain pozzolans is known to reduce early strength, and enhance strength at later ages. One of the practical problems associated with their inclusion is reduced heat of hydration, which in turn retards the hydration of C_3A and C_4AF, reducing early concrete strength (Plowman & Cabrera, 1984). Reduced heat of hydration can however be beneficial in some circumstances, such as in the construction of very large concrete structures, where regulated curing temperatures may be required (Beushausen, et al., 2011).

Concrete strength development with natural pozzolans is influenced by both specific surface area (SSA) and chemical composition (eg. $SiO_2 + Al_2O_3$). Pozzolan glass content and magma cooling rate also influence reactivity, and therefore concrete strength development (South, 2009). A selection of commonly used pozzolanic materials is briefly explored in the following sections, accompanied by scanning electron microscope (SEM) images in Figure 2.5.

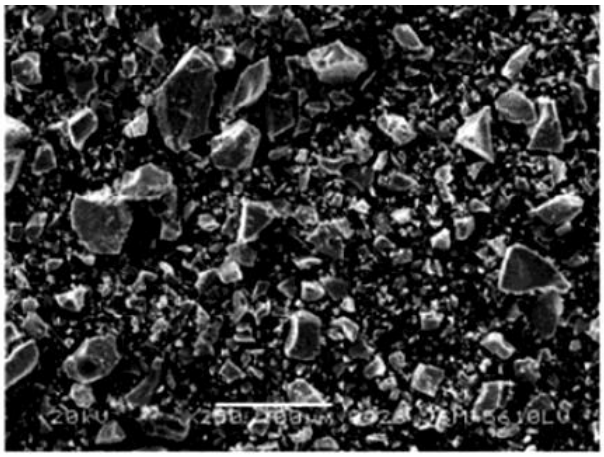
2.5.1 Fly Ash

Fly ash (pulverised fuel ash or PFA) is a by-product of coal fired power generation (extracted from flue gases) and is commonly used as a pozzolanic cement additive. Fly ash is also known to reduce concrete or mortar hydration heat, and retards the hydration of both C_3A and C_3AF (Plowman & Cabrera, 1984). The addition of fly ash can increased initial cement hydration rates, however it retards the dormant and acceleration periods. Retardation effects tend to be higher with higher water to binder (w/b) ratios (Langan, et al., 2002).

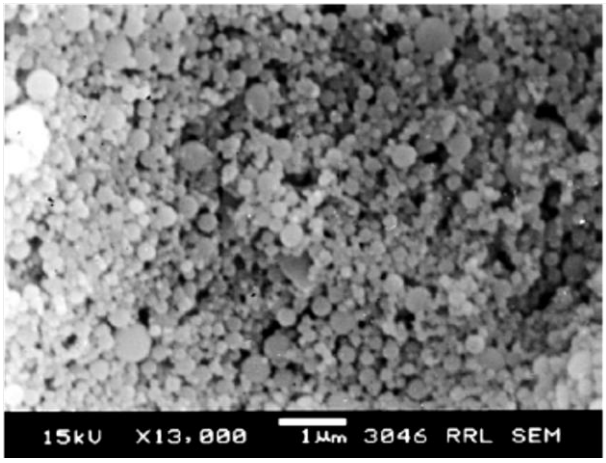
It is thought that the retarding mechanisms of fly ash are similar to those of gypsum. Its effectiveness can be explained by the rapid release and dispersion of both SO_3^{2-} and Ca^{2+} ions into solution; where its shape and surface properties enable a more efficient distribution of these ions than equivalent gypsum quantities (Plowman & Cabrera, 1984). High lime fly ash has been used in New Zealand cements in the past, and is again noted to significantly retard hydration. This is thought to be caused by its relatively high B_2O_3 content, which can be up to 1.8% (Kennerley, 1988).



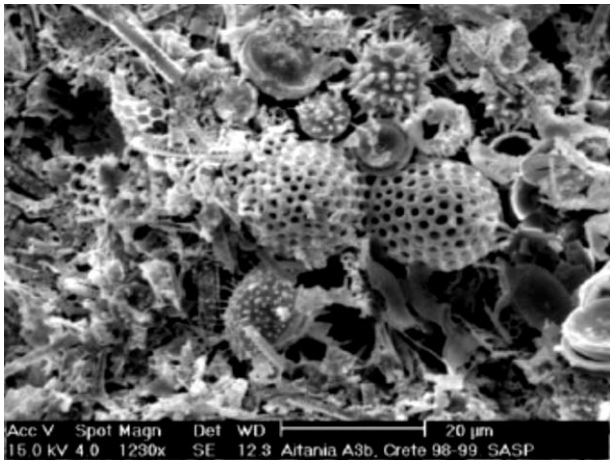
Fly ash (Siddique & Khan, 2011)



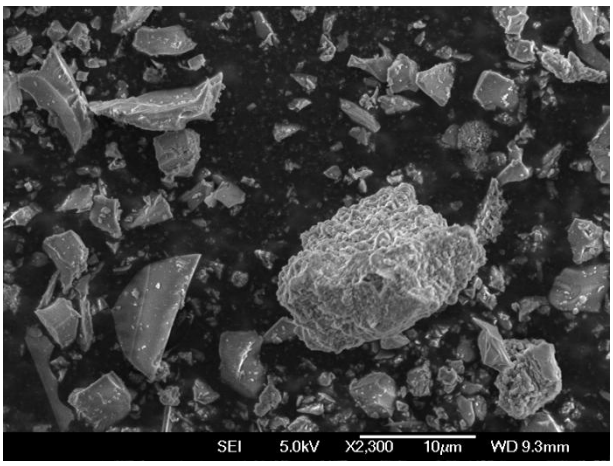
Ground granulated blast furnace slag (Chandrasekhar, et al., 2002)



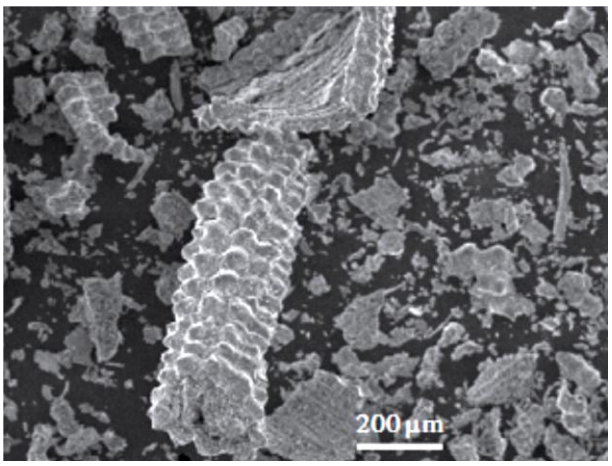
Silica fume (Yoon & Yun, 2006)



Diatomaceous earth (Stamatakis, et al., 2003)



Milled pumice



Rice husk ash (Ferraro & Nanni, 2012)

Figure 2.5: SEM images of typical pozzolans

2.5.2 *Ground Granulated Blast Furnace Slag*

Ground granulated blast furnace slag (GGBS) is a by-product of the iron and steel manufacturing processes, derived from metallic ore, gangue materials, and lime. Slag is a latent hydraulic binder, and hardens in the presence of alkalis such as calcium hydroxide (a product of Portland cement hydration). The use of slag as a supplementary cementitious material (SCM) results in reduced heat of hydration, increased durability, and increased long term strength, even at replacement levels as low as 10%. Compared to ordinary Portland cement (OPC), slag concretes have enhanced resistance to chloride attack and alkali silica reaction (ASR[1]), especially at replacement levels of 50% and above. Slag concretes are however more prone to carbonation, and can be more permeable (Beushausen, et al., 2011; Alexander, et al., 2003).

2.5.3 *Silica Fume*

Silica fume (SF) is a by-product of the industrial production of silicon or silicon alloys, where quartz is reduced in an electric furnace (Taylor, 1997). SF reduces concrete diffusivity by increasing density and reducing porosity, and also by producing a pozzolanic C-S-H gel with a relative diffusivity up to 25 times less than that of OPC. It can improve concrete strength and durability; however increased curing temperatures and autogenous shrinkage must be controlled to reduce early concrete cracking (Bentz, 2000).

A Canadian study by Langan et al., (2002) found that adding SF accelerates cement hydration at high w/b ratios. At low w/b ratios, SF initially retards hydration and prolongs the dormant period, however enhancing hydration at later stages. SF is also reported to enhance concrete tensile strength (Bhanja & Sengupta, 2005).

[1] The reaction between alkalis in cement and reactive silica in aggregates, causing concrete expansion and cracking (Multon, et al., 2009).

2.5.4 Natural Pozzolans

A range of natural pozzolans may be suited for use as a partial cement replacement, including many volcanic deposits, diatomaceous earths, and agricultural by-products[2]. Volcanic pozzolans are generally the result of explosive rhyolitic eruptions, which produce highly silicic lava and pyroclastic debris. Diatomaceous earths are sedimentary deposits consisting predominantly of fossilised silicic diatom frustules (external cell walls) (Stefano, et al., 2009). Agricultural by-products include ashes of rice husk, bagasse (sugar cane), and palm oil (Chatveera & Lertwattanaruk, 2009). Chemical and physical properties of individual pozzolans will vary, as will their suitability for use in concrete or mortar.

An Italian study of the addition of Roman natural pozzolan from Segni (volcanic) and Sacrofano (diatomaceous earth) by Collepardi et al., (1978) revealed several changes in C_3A hydration. They noted retarded hydration, particularly with the addition of the diatomaceous earth, and suggested this was the result of pozzolan adsorption onto C_3A grains.

In cement containing the Segni volcanic pozzolan, observations included a reduction in paste stiffness during the first 10-30 minutes of hydration, due to laminar hexagonal hydro-aluminate crystals transforming into cubic C_3AH_6. The study concluded that in addition to well known lime-pozzolan reactions, other complex reactions between pozzolana and C_3A (or its hydration products) also occur (Collepardi, et al., 1978).

Rice husk ash (RHA) is an agricultural by-product, where the husk is used as a fuel source in rice milling and electricity generation. RHA has pozzolanic properties broadly similar to those of SF. When burned under controlled conditions (350-600°C), RHA consists largely of amorphous silica, retaining the cellular microstructure of the original material. RHA was found by Chatveera & Lertwattanaruk (2009) to improve mortar resistance to attack from sodium sulphate, although reducing resistance to magnesium sulphate. The material has a

[2] For purposes of this summary, agricultural by-products are considered 'natural' pozzolans.

very high specific surface area (SSA), and can be even more reactive than SF (Chatveera & Lertwattanaruk, 2009; Taylor, 1997).

2.6 Mineralogical Analysis of Cement Hydration

Cement phase mineralogy incorporates a complex series of reactions involving many constituents. The most common method of quantifying phase minerals is using the Bogue calculation, which transforms elemental oxide composition (determined using wet chemical analysis or x-ray fluorescence (XRF)) into hypothetical mineral composition. This assumes stoichiometric phase compositions, and that thermal equilibrium is achieved in the kiln during the manufacturing process. This however tends to overestimate the belite content, and underestimate alite (Hewlett, 1998).

A refinement of this method, the Taylor-Bogue calculation, further accounts for the inclusion of guest-ions, which improves the quantitative prediction of the main clinker phases (Poulsen, et al., 2009). Due to the amorphous nature of the C-S-H gel and its variable stoichiometry, the kinetics of the hydration process can only be directly studied by quantifying the amount of non-reacted C_3S as a function of hydration time (Hewlett, 1998).

The suitability of x-ray diffraction (XRD) for quantitatively assessing phase mineralogy of hydrating cement is unclear. When cement is brought into contact with water, soluble solids such as gypsum dissolve and semi-equilibrate with the pore solution. Clinker phases hydrate at different rates, continuously releasing Ca, Si, Al, Fe and hydroxide into solution, eventually precipitating as C-S-H, ettringite, and other hydrate phases (Lothenbach, et al., 2008). Because of their semi-amorphous nature, cement hydration products do not display clear XRD peaks (Kakali, et al., 2000).

Hesse et al., (2011) report that the progress of cement hydration can be measured using a combination of heat flow calorimetry and XRD analysis. Heat flow calorimetry is useful in determining the heat evolution of hydration, while XRD analysis is useful in measuring time dependent phase composition. XRD is also identified by Cuberos et al., (2009) as an appropriate technique to identify and quantify the crystalline phases in cement. Where the

Rietveld methodology (line profiling using methods of least squares) is applied, quantification of amorphous phases is also possible. However, given the complex reactions occurring in cement hydration, the method is not straightforward (Hesse, et al., 2011).

Experimental methods for quantitative phase analysis include XRD, combined with Rietveld analysis, and optical point counting. The quantification of alite and belite using the XRD approach is complicated by overlap of the respective high intensity reflections. Point counting is tedious, and relies heavily on the skill of the operator (Poulsen, et al., 2009). Nuclear Magnetic Resonance (NMR) is an alternative method for quantifying phase composition, and has the ability to detect both crystalline and amorphous hydration products. Poulsen et al., (2009) found that NMR proved a valuable tool in quantifying alite and belite content in anhydrous cement containing low-moderate levels of iron (<5% wt). The study included a comparison with XRD-Rietveld phase analysis, and found that quantities of alite and belite calculated using NMR were slightly higher and lower respectively than those calculated by XRD-Rietveld.

Chapter 3 Natural Pozzolans

3.1 Natural Pozzolans in New Zealand

New Zealand is situated on the boundary of the Australian and Pacific tectonic plates; hence it experiences a high level of geological activity. An extensive variety of natural pozzolans are readily available in New Zealand, including include pumice, tuff, breccia, rhyolite, diatomaceous earth, and amorphous silica (Hastie, 2009).

Research into New Zealand's natural pozzolans dates back to at least 1937, when Henderson investigated 43 natural materials across the country. Pozzolanic activity was determined using a lime absorption test, and it was loosely determined that several local materials presented promising results. Interest in local natural pozzolans was renewed post World War II, when demand for cement in New Zealand exceeded local supply. The addition of natural pozzolans was identified as one way in which this shortage could be overcome. In 1949, the San Francisco symposium on the use of pozzolanic materials in mortars and concrete detailed the advantages of using pozzolanic additives. These included reduced heat generation, improved workability, and improved resistance to expansion and cracking due to alkali-silica reaction (ASR) (Kennerley & Clelland, 1959).

Unmilled pumice from Takanini with a specific surface area of 300m^2/kg was used in a large sewerage project in the 1950's due to its resistance to sulphate and acid attack (Kennerley, 1988). Later, with the establishment of hydro-electric power generation along the Waikato River, more detailed qualitative testing was undertaken on a range of New Zealand natural pozzolans. From this extended investigation, it was established that pumice and diatomite were superior to other basic materials such as andesite, ignimbrite and basaltic tuffs. Efforts were then focussed on concrete testing with additions of pumice from Mangakino and Kaimai, and diatomite from Whirinaki and Middlemarch. The Kaimai pumice was the first of these to be commercially used in concrete in one of the Waikato hydro-electric projects (Kennerley & Clelland, 1959).

Pumice was used as a concrete additive in the construction of several Tongariro and Waikato Rivers hydro and geothermal power stations until the early 1970's. In 1985, pumice from Ohaaki was used in the Ohaaki geothermal power station to improve concrete resistance to CO_2 and H_2S attack. Fly ash from the Genesis Energy coal fired power station at Huntly has attracted commercial interest, and other large projects such as the Clyde Dam explored the possibility of using calcined marl and oil shale as concrete additives (Kennerley, 1988).

A further investigation into the use of New Zealand's natural pozzolans in concrete manufacture was undertaken by Milburn NZ Ltd in 1988. This study identified slag, fly ash, silica fume, pumice, diatomite, geothermal silica and amorphous silica as the more commonly available materials. At the time of publishing, all except silica fume were being produced or found naturally within New Zealand (Waelen, 1988).

3.2 Taupo Pumice

The Taupo pumice (formally named the 'Taupo Lapilli Member of the Taupo Pumice Formation') is a Holocene pyroclastic unit widely deposited in the Taupo Volcanic Zone (Figure 3.1). The eruption was a multiphase eruptive sequence, consisting of Plinian and Phreatomagmatic volcanism (Walker, 1980). The eruption is dated at 1718 ± 5 years B.P. (Hogg, et al., 2011).

Pumice is a product of explosive volcanism, and consists of highly vesicular silicic to mafic glass foam. Most pumice has a density <1.0g/cm3, and will therefore float on water until it becomes waterlogged. Pumice behaviour in the sedimentary environment is influenced by its low density and buoyancy, and following eruptions, pumice can travel the globe on oceanic currents. Due to its low density, pumice grains are able to travel further in fluvial environments than denser clastic materials with the same grain size (Manville, et al., 1998).

The Taupo Volcanic Zone (TVZ) is situated in the central North Island, and is approximately 300km long. The area is associated with intense, dominantly silicic Quaternary volcanism, extensional normal faulting, and is one of the worlds most frequently active zones of rhyolitic volcanism. Numerous, caldera-forming eruptions have occurred in the area, with two presently active centres in Okataina and Taupo (Manville et al., 2005; Smith et al., 2005).

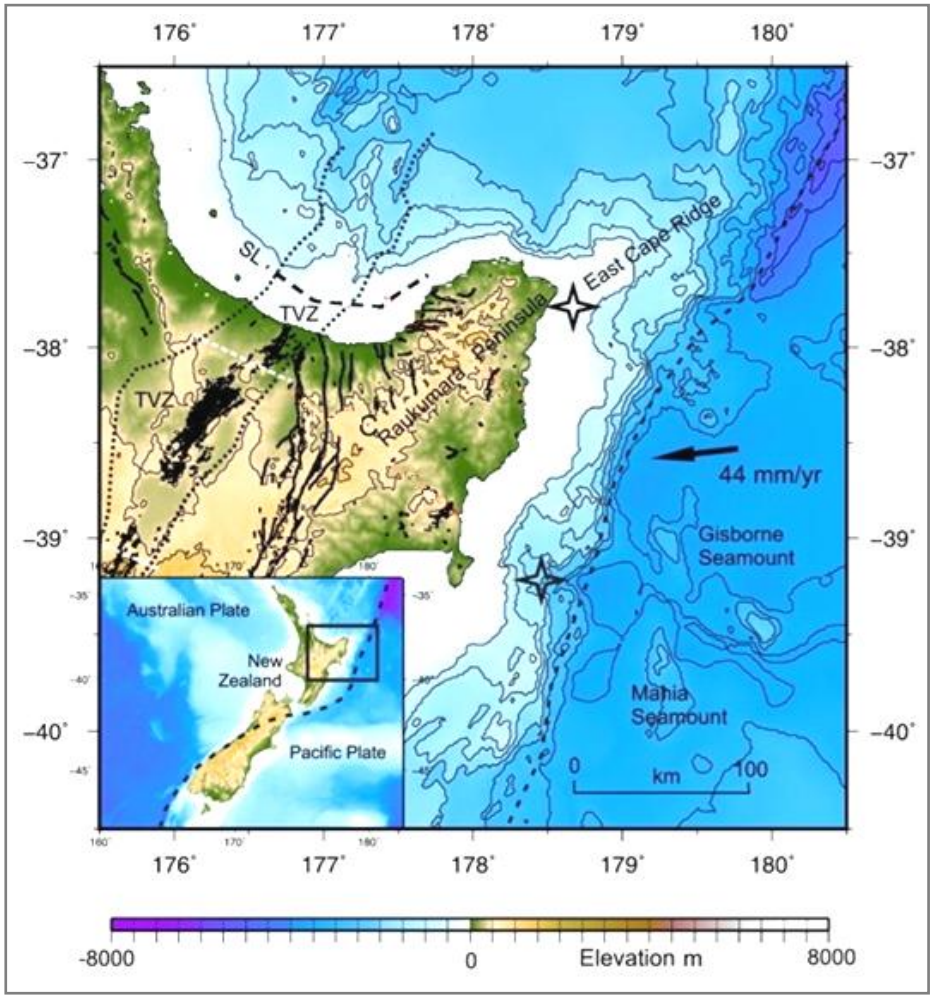


Figure 3.1: Taupo volcanic zone and regional setting
(Adapted from Darcey & Ristau, 2011)

Taupo deposits are generally crystal poor, ranging between 1-15% crystals. Glass composition of Taupo rhyolitic deposits range between 74.6-78.3 wt.% SiO_2, 0.6-1.8 wt.% CaO, and 2.7-4.6 wt.% K_2O (Smith, et al., 2005).The most recent Taupo eruption resulted in the emplacement of approximately 30km^3 of pyroclastic density current ignimbrite across a 20,000km^2 radially dispersed area. This density current entirely devastated vegetation in the area, the charred remains of which can be seen in the ignimbrite itself (Manville, et al., 2009).

The ignimbrite is entirely non-welded, and is composed of materials with significantly different granulometric and hydrodynamic properties. The bulk of remobilised material consists of pumiceous debris (Manville, et al., 2009). Large volumes of pyroclastic material were eroded and remobilised, which was then deposited in the beds of the Waikato River. Deposits are particularly thick where the river is confined by walls of incised country rock or

Quaternary fluvial terraces. Coarse grained, cross-bedded crystal/lithic rich sands and gravels tend to dominate close to the valley axis, with material fining laterally into more pumiceous sediments (Manville, et al., 2009).

3.3 Investigation of Taupo Pumice from Horotiu

In 1998 an investigation of Taupo pumice was undertaken using a sample from Horotiu, Waikato (hereby referred to as 'Horotiu pumice'), by Milburn (NZ) (now Holcim (NZ) Ltd). The trial involved milling 80 tonnes of dried pumice through Cement Mill 2 (a ball mill) at the Westport Cement Works, testing a variety of cement-pumice blended concretes (Brown, 2010). Milled 'Horotiu pumice' particle size distribution (PSD) is provided in Figure 3.2.

This pumice has similar chemical and physical characteristics to that sampled from Rangiriri, however Horotiu is approximately 30km upstream, closer to source. This may influence material quality, where the downstream material (Rangiriri) may be have undergone more reworking, accumulating more clays and organics (depending on local depositional conditions). These materials are generally deleterious to concrete performance.

Concrete trials were conducted in 1998, adding 'Horotiu pumice' to various 17.5MPa, and 30MPa mixes (Brown, 2010). The mixes of greatest interest to this project are the 30MPa concretes listed in Table 3.1. The latter four mixes replaced cement at 20% and 30% respectively, incorporating a 50% oversubstitution[1] of pumice. Concrete strengths from these trials are presented in Figure 3.3, where mixed results are recorded. Some mixes return significant reductions in strength at 28 days (10-32%), where others achieve parity or exceed the General Purpose (GP) reference (Figure 3.4). The good performance of the 20% pumice mix with 50% oversubstitution is particularly notable, where the performance of both mixes containing superplasticiser (Euco SP and 1000R SP) are particularly poor (Brown, 2010).

[1] In these mixes, additional unmilled pumice was added in place of sand, effectively adding more binder to the mix.

Table 3.1: 1998 'Horotiu pumice' concrete mix descriptions

Mix Description
30MPa Standard
20% Pumice
30% Pumice
20% Pumice + 50% oversubstitution
30% Pumice + 50% oversubstitution
30% Pumice + 50% oversubstitution + Euco SP
30% Pumice + 50% oversubstitution + 1000R SP

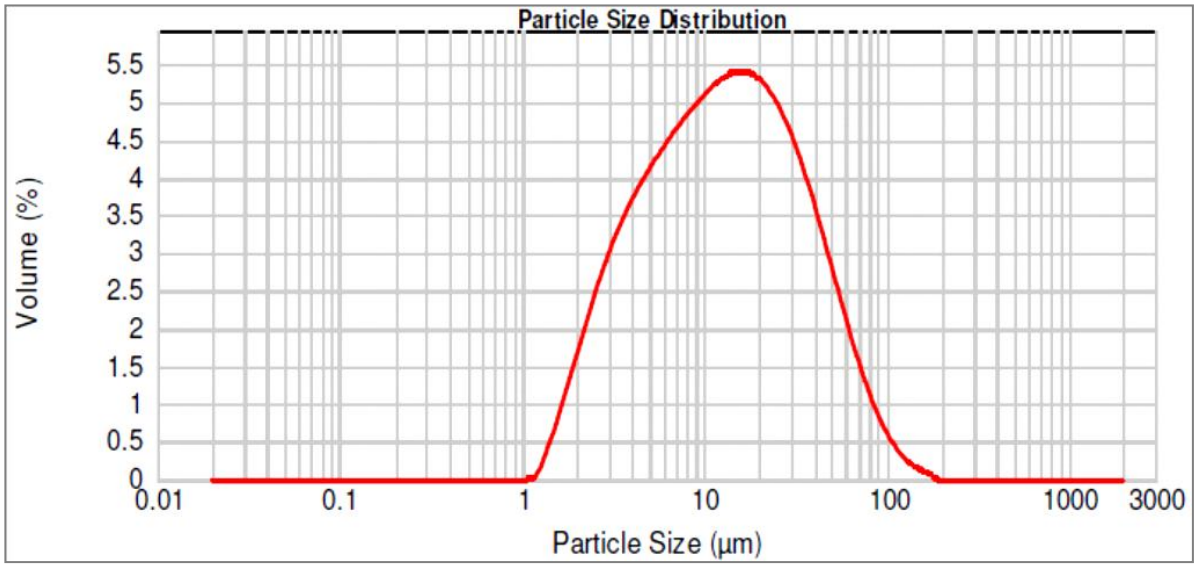


Figure 3.2: 'Horotiu pumice' PSD

X-ray diffraction (XRD) results for pumice from Horotiu and Rangiriri are provided in Appendix 1 and Appendix 2. Of the crystalline material in the 'Horotiu pumice' sample, quantitative estimates of 65% albite and 35% calcite have been made.

These estimates are unlikely, as calcite is not expected to form a significant portion (if any) of Taupo pumice. As this pumice was processed in a cement mill, and later handled at a cement packing plant, there is potential for contamination from potentially significant cement residue. Therefore, concrete strengths may be influenced not only by the pumice, but an unknown quantity of cement. This has effectively been interground with the sample, potentially giving artificially high strength results. New XRD analyses of fresh pumice samples from Horotiu (tested as part of this study) support this conclusion, as no calcite was detected in either of the two spot samples (Appendix 3).

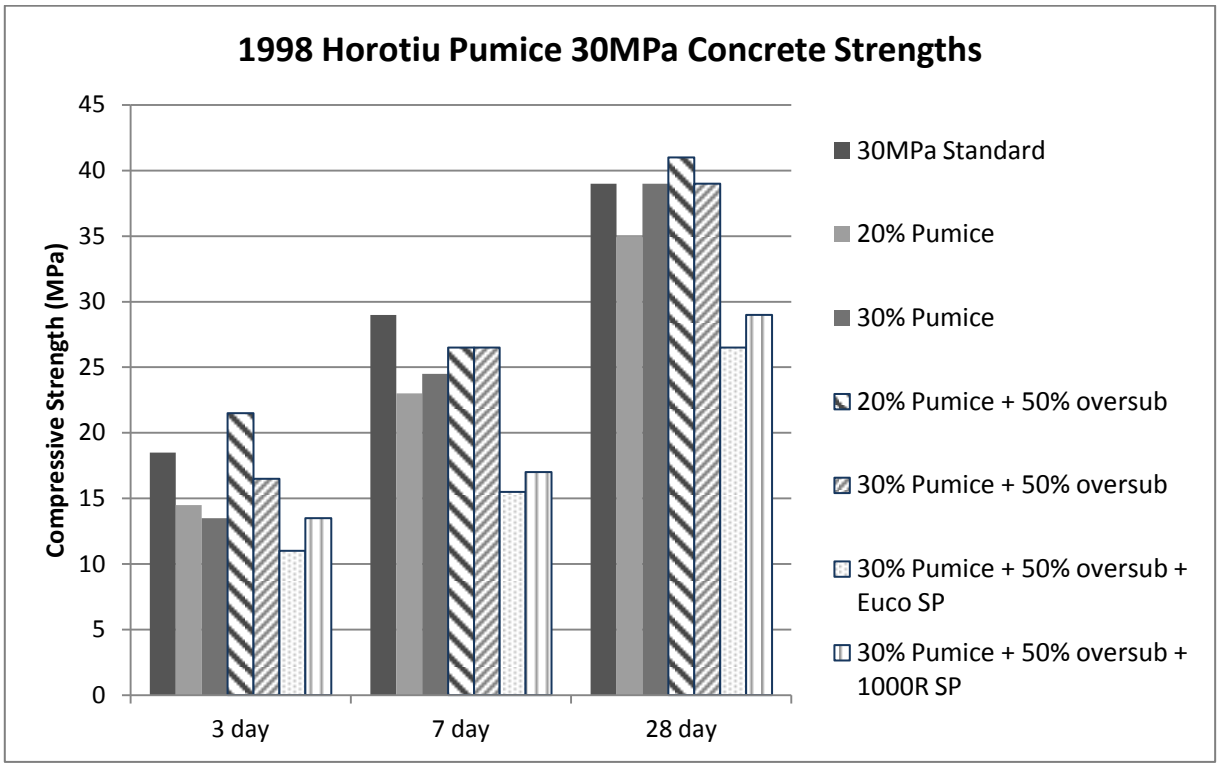


Figure 3.3: 'Horotiu pumice' 30MPa concrete strength

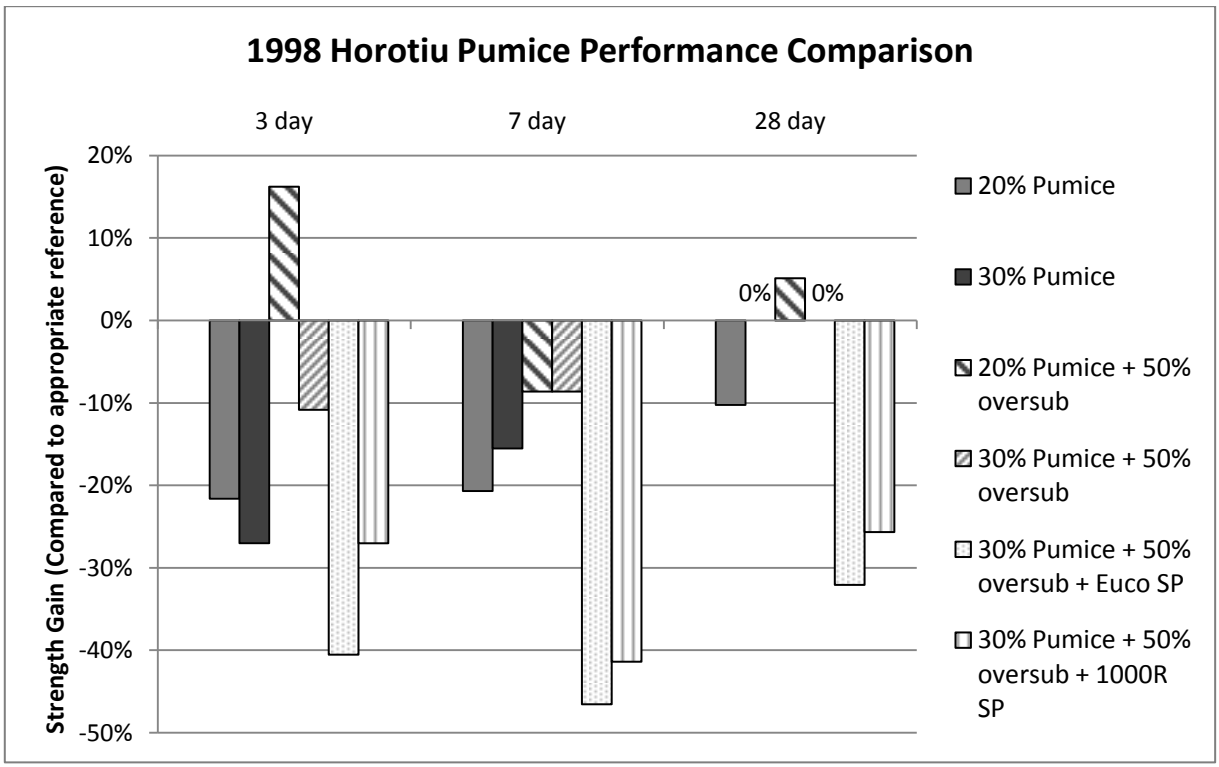


Figure 3.4: 'Horotiu pumice' 30MPa concrete performance comparison

3.4 Pozzolanic Activity

The term 'pozzolanic activity' refers to the maximum amount of lime that a pozzolan can combine with, and the rate at which this occurs. The amount of lime combined with pozzolan is controlled by five main factors (Hewlett, 1998):

- The nature of the active phases
- Their content in the pozzolan
- Their SiO_2 content
- Lime/pozzolan ratio
- Length of curing

Hewlett further identifies three factors which determine the combination rate:

- Pozzolan Specific Surface Area (SSA)
- Water/solid ratio
- Temperature

A number of tests for reporting pozzolanic activity have been reported throughout the literature. Direct methods monitor the presence of $Ca(OH)_2$ and its depletion over time as the pozzolanic reaction proceeds, using either thermo-gravimetric analysis (TGA), x-ray diffraction (XRD) or titration. The Frattini test is a commonly used method, where Ca^{2+} and OH^- concentrations in a solution of Portland cement and the test pozzolan are determined by titration. The saturated lime method is similar, but slaked lime ($Ca(OH)_2$) is used instead of Portland cement. Indirect methods involve measuring physical properties such as compressive strength, electrical conductivity or heat evolution (Donatello, et al., 2010).

Concrete strength testing has always played an important role in the development of supplementary cementitious materials (SCM's). Tests have traditionally used mortar; however the correlation between Ultracem mortar and concrete strengths have proved unreliable[2].

[2] This is based on advice from senior analysts of the Holcim NZ Technical Department.

Methods of determining pozzolanic activity (such as the pozzolanic activity index with Portland cement) were heavily scrutinised during the late 1980's, and following several round-robin studies, changes in the test method were initiated. These included a recommendation that any test conducted at ambient temperatures for less than 28 days was not suitable for assessing the pozzolanic nature of the material, as it only identified how the material performs in concrete. The strength activity index test with lime was controversial due to poor (and somewhat unexplained) inter-laboratory comparability. It was ultimately determined that the method was as much a test of the lime (purity, fineness etc) as it was of the SCM (Lamond & Pielert, 2006).

Given the wide and complex variation in pozzolan types, a generic model of pozzolanic activity is difficult to define, although general trends can be identified. The larger the amount of combined lime-pozzolan, the higher the active phase content, and the lower the content of inert or crystalline phases (eg. quartz, magnetite, sanidine etc). Lime combination is related to the SiO_2 content in the active phases, which in volcanic glass ranges between 45-75% (Hewlett, 1998). Pumice from Rangiriri used in this investigation is ~70% amorphous (see Section 7.8.1).

Hewlett (1998) reports that within certain limits, the amount of combined lime increases as the lime/pozzolan ratio increases. Within 28 days, pozzolans containing 50-60% silica are capable of chemically binding with approximately two thirds of the original lime. This varies widely between pozzolans, and at 91 days, lime-pozzolan combination is essentially complete (whereas lime-fly ash combination is quite incomplete).

Further testing (eg. South, 2009) suggests that short term pozzolanic activity is highly dependent on SSA, where longer term activity is more dependent on the chemical and mineralogical composition of the pozzolan. The reaction rate is reported to be proportionate to the square of SSA (Hewlett, 1998). Targan et al., (2003) also tested a range of natural pozzolan-cement blends (Figure 3.5). In this study, researchers attributed reductions in strength at Natural Pozzolan (NP) additions of 15% and above to a surplus of fine material. This moves cement grains apart, causing unpacking of the system and a considerable decrease in strength (Targan, et al., 2003).

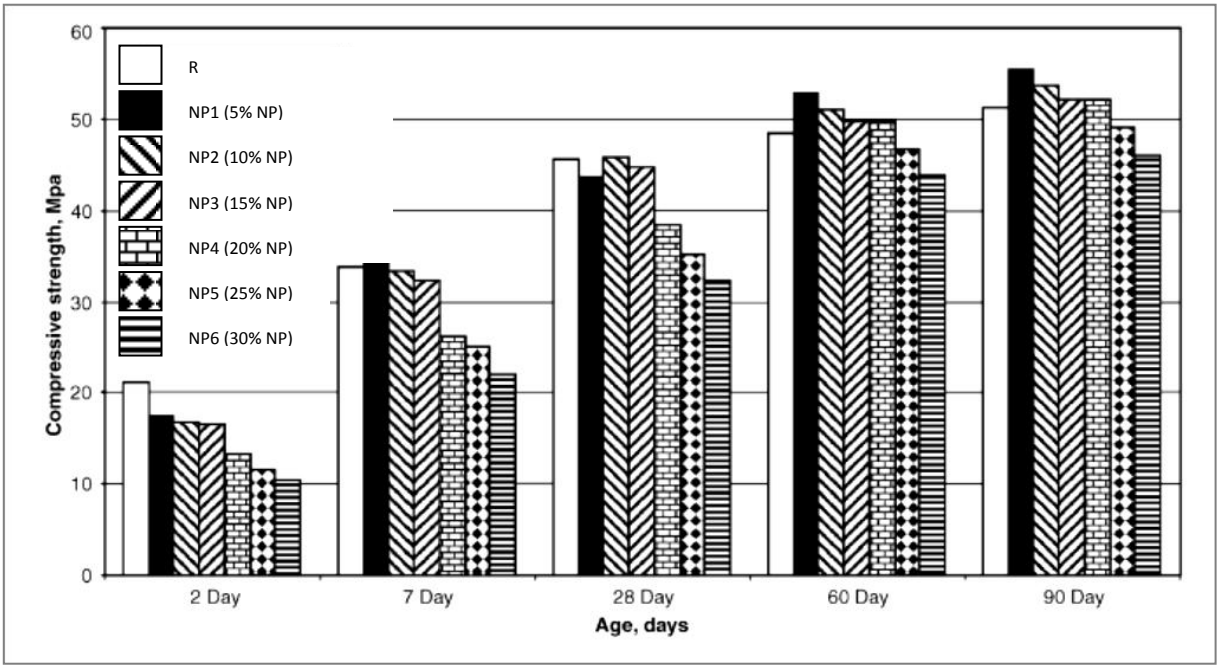


Figure 3.5: Composite concrete strength
(Adapted from Targan et al., 2003)

3.5 Particle Fineness

Particle size distribution (PSD) is a key parameter in both the pozzolan and the cement itself. Increasing fineness generally results in increased early strength gain, and cements with a narrower PSD generally result in higher strength concrete or mortar (Binici, et al., 2007). Zhang & Napier-Mumm (1995) note that although concrete strength increases with cement specific surface area (SSA), cement fineness is more effective at early stages (1-3 days) than at later stages (28 days). They also note that cements with equal SSA may have significantly different PSD.

The amount of hydration products formed at the beginning of curing depends on the solid surface area upon which water can react. Across a range of cement specific surface areas, an increase of 1% in surface area results in approximate strength increases of 2% at 7 days and 1% at 28 days. A study of German cements found that the 0-3µm cement fraction achieved particularly high 1 day strength, and the 3-25µm fraction achieved the highest 91 day strength. The 25-50µm fraction achieved the lowest strength gain up to 28 days, and only after 91 days did this fraction achieve similar strengths to that gained by the 0-3µm fraction. To attain higher 28 day strengths, a higher portion of the 3-25µm fraction was needed.

Particles greater than 60µm have only a 'filling' effect, and make negligible contributions to concrete strength (Zhang & Napier-Mumm, 1995; Celik, 2009).

Although the correlation is not direct, the water demand for a concrete of a given workability and the apparent reactivity of the pozzolan are both dependent on fineness. Measuring fineness accurately is therefore a key parameter of any study involving particulate matter. The American Society for Testing Materials (ASTM) initially published specifications for determining fineness of SCM's using Blaine specific surface area (SSA). Debate as to which method should be used led to the mean particle diameter being substituted as the standard test method in 1965, however SSA was reinstated in 1968. This carried the additional requirement of wet sieving, with a limit of 12% retained at 45µm. The percentage retained at this fineness does not measure the fine material that is actually contributing to the concrete strength reactions, but does indicate the amount of fine material present (Lamond & Pielert, 2006).

Specific Surface Area (SSA) is an important property of powdered material, and is a useful indicator of its reactivity. To determine SSA, the cement industry has traditionally used the Blaine method, which measures the time for a specific volume of air to flow through a known volume of compacted powder. This, combined with the materials density is used to calculate SSA (Potgieter & Strydom, 1996).

To determine the fineness (and therefore reactivity) of materials, the cement industry has now moved away from the traditional Blaine surface area measurement, instead opting for laser diffraction particle size analysis. Cements with equal specific surface area may have quite different PSD's, therefore specific surface area can be a somewhat misleading measure of fineness (Zhang & Napier-Mumm, 1995).

3.6 Kairiri Farms – Rangiriri

The Kairiri Farms Ltd site at Rangiriri, Waikato, was identified as a potential commercial source of pumice by Holcim NZ. This assessment was based on resource size, material quality, and proximity to market. The farm is situated near the historically significant Rangiriri Pa, the site of a major Maori land battle (Brown, 2002)

Land use is currently divided between dairy farming and crops. The site lies on the floodplains of the Waikato River, 600-700m west of the present main channel with an average thickness of 5-6m (Holcim NZ, 2010). Pumice has been historically mined in small quantities from the Rangiriri site for use as an insulating building material. The outcrop sampled and milled for use in this thesis is shown in Figure 3.6.

Figure 3.6: Pumice outcrop sampled for Loesche milling

Chapter 4 Concrete Durability With Pozzolans

A wide body of literature is available regarding concrete durability with natural pozzolans, with significant variation in results between studies. The nature and composition of pozzolans, whether natural or man-made, is inherently variable. The chemistry and mineralogy of natural deposits depends on factors such as host magma geochemistry and post depositional contamination, where the composition of fly ash and slag will vary between industrial facilities. Therefore, it is not surprising that durability analyses conducted worldwide sometimes appear to contradict each other. This chapter is not intended to present definite conclusions regarding any particular pozzolan, rather presenting a holistic summary of relevant research.

Durable concrete has the ability to resist destructive environmental forces without excessive maintenance. Many factors influence concrete durability and rebar corrosion, including the influence of chloride ion and concrete carbonation, pore solution chemistry, concrete mix design, and curing conditions. In addition, local variations in aggregate type, exposure conditions, and raw material mineralogy can have a significant influence on concrete and rebar corrosion rates (Morris, et al., 2002). Concrete durability is a property not adequately measured using any one test, instead a range of tests are employed to indicate durability parameters (Wong, 2001).

Pozzolans can reduce the susceptibility of concrete to attack from the environment through a reduction in concrete permeability and ion diffusivity. The resistance of concretes to acidic waters can increase, and the diffusion of aggressive ions (eg. chloride) can be reduced. Effects are generally proportional to pozzolan replacement levels (Hewlett, 1998). Additionally, blended concretes made using superplasticiser can be considerably more durable than those made without (Çolak, 2003).

A UK study by Kahn & Lynsdale (2002) investigated the effects of adding silica fume (SF) and fly ash (pulverised fuel ash or PFA) to high performance concrete. The commercial addition of silica fume has become increasingly popular due to its extreme fineness and high

pozzolanicity. This produces a low permeability concrete, however superplasticiser is essential for maintaining a workable paste.

Hewlett (1998) presents a summary of concrete durability with fly ash. In this, the addition of fly ash reduced concrete permeability, especially at later ages. Resistance to sulphate attack was increased, and the coefficient of chloride diffusion significantly reduced. Resistance to alkali silica reaction (ASR) was generally improved, however no significant reduction in chloride or carbonate induced corrosion, or freeze thaw resistance was reported. He further summarises the effect of microsilica addition to concrete, where the main effect on durability was through the significant reduction in permeability. Overall, durability was improved against most chemical and physiochemical attacks (Hewlett, 1998).

Adding slag or fly ash to concrete is known to delay the onset of corrosion by reducing the rate of chloride ingress (Polder & Peelen, 2002). Fly ash is not widely available in New Zealand, and due to opposition to coal fired power stations, future local supply is not likely to significantly increase. For this reason, fly ash is not likely to present a viable commercial option as a widespread cement replacement in New Zealand concretes. The addition of milled pumice is therefore investigated as not only a more economic and environmentally sustainable partial cement replacement, but as a commercial option for the production of highly durable concrete. Properties relating to the durability of blended concretes are explored in the following sections.

4.1 Chloride Attack

The most severe corrosion of concrete steel reinforcing is caused by chloride ion ingress. When chloride ions come into contact with steel reinforcing, rapid spalling of the surrounding concrete occurs, making it easier for chloride to penetrate the second and subsequent steel layers (Zuquan, et al., 2007; Aitcin, 2003). This can occur where concrete is exposed to the marine environment, de-icing salts, or prepared with contaminated aggregates (Morris, et al., 2002).

Chloride ingress occurs dominantly as a result of diffusion, and the chloride diffusion coefficient can be calculated using the bulk diffusion test. In this test, chloride ions are allowed to penetrate the concrete specimen, as per the principles of Fick's second law of diffusion[1]. The chloride diffusion coefficient defines the capacity of a concrete to resist chloride penetration, and can be used to predict the service life of a reinforced concrete structure (Lizarazo-Marriaga & Claisse, 2009). Although the diffusion coefficient reduces as the concrete continues to hydrate, this is not normally considered in the bulk diffusion test (Stanish & Thomas, 2003) .

4.2 Wet-Dry Cycles

Wet-dry cycles can also deteriorate concrete, especially in brackish waters with high salinity. Sea water is particularly harmful to concrete, and when combined with other components of marine systems (such as tides, storms, freeze-thaw, wet-dry, and corrosion), concrete can be aggressively attacked. Salt precipitates and accumulates in voids, attacking steel reinforcing and chemical bonds within the concrete (Toutanji et al., 2004; Aitcin, 2003). Zones of concrete alteration in the marine environment are presented schematically in Figure 4.1.

[1] Fick's second law of diffusion describes the non-steady state diffusion of atoms (Askeland, et al., 2010).

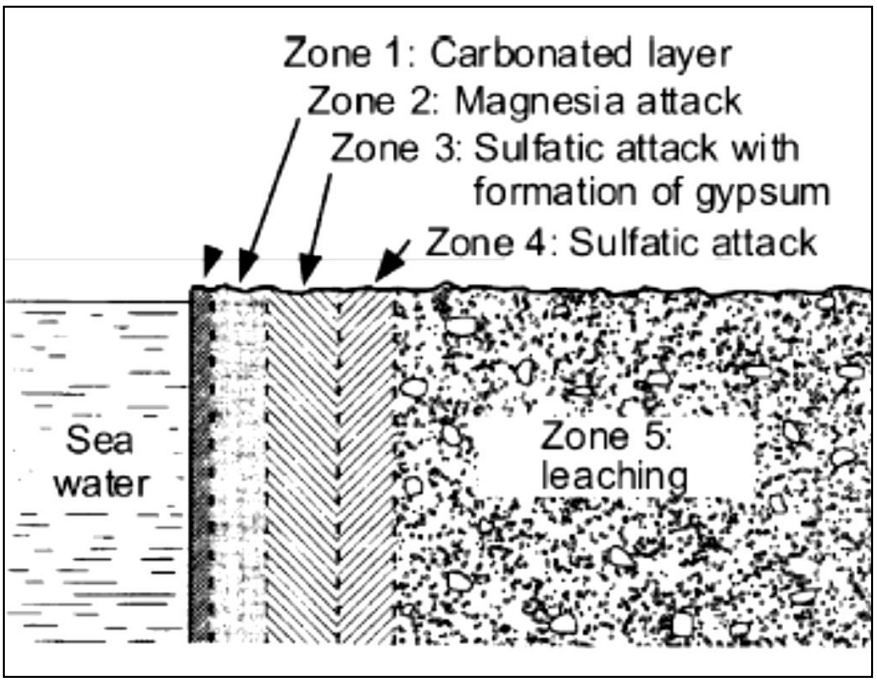


Figure 4.1: Concrete alteration zones in the marine environment
(Aitcin, 2003)

4.3 Carbonation

Carbonation is another common cause of steel deterioration in concrete, especially with inadequate concrete cover depth. Carbonation occurs where atmospheric carbon dioxide (CO_2) dissolves in cement pore solution and forms carbonic acid (H_2CO_3). CO_2 reacts with all phases of hydrated cement, including calcium hydroxide and the C-S-H gel. The resultant carbonic acid reduces pore solution pH, and neutralises solid alkaline phases.

As alkaline solids are depleted, a carbonated low pH zone extends from the surface into the concrete, forming calcium carbonate in cracks and on the concrete surface. Cracks which result from tensile stresses also increase carbonation depth (Newman, 2003; Çolak, 2003).

The reported influence of pozzolans on concrete carbonation varies substantially. Kaid et al., (2009) report that blended concretes are often less resistant to carbonation, due to reduced calcium hydroxide content. However, Çolak (2003) reports that soluble calcium hydroxide can be changed to relatively insoluble calcium silicate hydrate phases with the addition of natural pozzolan, improving durability characteristics.

As with other chemical degradation, effects can be significantly reduced by decreasing concrete permeability. However, Khan & Lynsdale (2002) found that while carbonation increased in concrete containing fly ash, little variation was reported with the addition of silica fume. Newman (2003) found that the addition of fly ash or ground granulated blast furnace slag substantially reduced paste alkali reserves, reducing resistance to carbonation.

4.4 Sulphate Attack

Concrete can be attacked by naturally occurring sulphates of sodium, magnesium, potassium and calcium. These can be found in some soils and groundwater, and can damage concrete when in solution (Woodson, 2009). Sulphate attack is caused by two principal reactions; Na_2SO_4 and $Ca(OH)_2$ forming gypsum; and the reaction of this gypsum with calcium aluminate hydrates to form ettringite (Zuquan, et al., 2007).

Magnesium sulphates are particularly aggressive, reacting with all cement compounds (including C-S-H). This precipitates gypsum and ettringite, resulting in expansion and cracking. C-S-H is progressively degraded through the formation of gypsum, brucite ($Mg(OH)_2$) and hydrated calcium-magnesium silicate (C,M)-S-H, where calcium is partially replaced by magnesium (Zuquan, et al., 2007; Kaid, et al., 2009). This was also found by Hossain & Lachemi (2006), where blended concrete suffered advanced deterioration relative to OPC after 48 months of sulphate attack. This was attributed to the consumption of portlandite by the pozzolanic reaction, causing Mg^{2+} cations to react with C-S-H gel, producing a porous, cohesionless M-S-H gel.

Resistance to sulphate attack is particularly dependent on cement C_3A and C_4AF content (see Section 2.4) (Hossain & Lachemi, 2006). Sulphate resistant cements (such as those used in oil wells), have relatively high ratios of Fe to Al. Chemically, these clinkers show substantial replacement of Al^{3+} as well as (or instead of) Fe^{3+} in the C_4AF phase (Taylor, 1997).

Kaid, et al., (2009) found that the addition of natural pozzolans could be optimised to improve protection from sulphate attack. However, Çolak (2003) found that sulphate resistance decreased significantly with increasing addition of natural pozzolan. The reduction

was attributed to the reaction between calcium hydroxide (released during OPC hydration) and aluminates (from both OPC and the pozzolan), producing ettringite, and subsequent expansion cracking (Kaid, et al., 2009; Çolak, 2003).

4.5 Freeze-Thaw Cycles

Freeze-thaw cycles can deteriorate concrete over a relatively short time span due to internal hydraulic and osmotic pressures generated by expanding water. As pressures increase, micro-fractures develop, and when the tensile strength of the paste or aggregate is exceeded, these eventually rupture (Morris, et al., 2002). This is particularly important in areas where concrete is exposed to extreme temperature variations such as Canada and northern Europe, but does have limited application in some areas of New Zealand.

Concrete freeze-thaw resistance depends on several parameters, most importantly concrete strength, porosity and the degree of pore saturation. With the addition of natural pozzolans, the reactivity of the pozzolan is of additional significance. Studies conducted by Çolak (2003) show that concretes blended with 30% and 40% natural pozzolan suffer significant degradation when subjected to repeated freeze thaw cycles, and that increasing pozzolan content results in further reductions in durability.

4.6 Electrical Resistivity

Concrete electrical resistivity is a useful measure of durability. Both theoretical and experimental works indicate a correlation between concrete resistivity and chloride ingress, where the chloride diffusion coefficient is inversely proportional to concrete resistivity (Polder & Peelen, 2002). Following the initial mixing of water and cement, water which was originally situated between cement particles gradually becomes a highly conductive pore fluid due to the dissolution of cement calcium and alkali ions. The main product of cement hydration is the C-S-H matrix, which is eventually disseminated with nanometre sized pores filled with this conductive fluid. Calcium hydroxide (another hydration product) forms crystals, and acts as an insulator (Coverdale, et al., 1995).

Concrete electrical resistivity can vary from 10^1 to 10^5 Ωm, depending on moisture content and concrete composition. Current is carried within the concrete by ions in pore solution. An increase in pore saturation, and an increase in the number of larger diameter pores (eg. higher w/b ratios) results in decreased resistivity. The addition of slag, fly ash, and silica fume can all increase resistivity due to the reduction in concrete porosity (Polder & Peelen, 2002).

4.7 Porosity and Permeability

Concrete pore systems consist of four pore types. These are: (1) gel pores, micro-pores with characteristic diameters of 0.5-10nm; (2) capillary pores, meso-pores with average diameters of 10-10,000nm; (3) macro-pores due to entrained air; and (4) macro-pores due to insufficient compaction. Capillary pores and macro-pores are responsible for reductions in concrete strength (Kumar & Bhattacharjee, 2003).

Milled Taupo pumice pores are generally tubular and elongated, with diameters which appear to fall in the range of meso-pores (see Section 5.4). As such, it could be inferred that while these pores are not likely to have an adverse effect on concrete strength, they may still contribute substantially to concrete porosity.

The spatial distribution of capillary pores controls concrete permeability, and therefore has a major influence on concrete durability (Coverdale, et al., 1995). Very fine particles (such as those of milled pumice or silica fume) can reduce concrete porosity, and may improve concrete durability at higher w/b ratios. Pozzolanic cement pastes actually have a higher total porosity than Ordinary Portland Cement (OPC) pastes at early ages, however capillary volume decreases with time. The rates at which this occurs depend on the nature of the pozzolan itself (South, 2009).

In terms of physiochemical degradation, concrete durability generally increases with reduced permeability. High performance concrete with a water/binder ratio (w/b) of 0.3-0.4 is usually more durable due to reduced porosity, and reduced capillary and pore network interconnectivity. This is due to the development of self-desiccation, where water moves

from pre-existing capillaries to the microscopic pores created during cement hydration (Aitcin, 2003).

Concrete permeability is an indication of the ease in which fluids, gases, or harmful ions can permeate through interconnected pores. These include chloride, oxygen, carbon dioxide and moisture, each of which are known to corrode steel reinforcing. Many factors influencing concrete durability are closely linked with porosity and permeability, including freeze-thaw, chloride and sulphate attack, and alkali silica reaction (ASR). The permeable porosity of concrete diminishes as the concrete cures, and is reduced at lower w/b ratios (Safiuddin & Hearn, 2005).

If concrete porosity is high but pores are discontinuous, permeability will remain low. Entrained air in concrete generally forms discrete, spherical bubbles with diameters approximately 50μm, which contribute little to increased permeability (Kearsley & Wainwright, 2001; Safiuddin & Hearn, 2005). Entrained air in concrete used throughout this research is <3% (see Section 7.12). Concrete porosity generally increases with the addition of natural pozzolans (Çolak, 2003), although can reduce with prolonged curing.

The American Society for Testing and Materials (ASTM) gives three methods for testing concrete porosity, using cold water, boiling water, or vacuum saturation. Effective saturation of the concrete specimen is critical in order to determine the permeable porosity, and each of the above methods were compared by Safiuddin and Hearn (2005). In this study, it was found that the vacuum saturation method was most effective in measuring dead-end pores[2] and air voids, and was their recommended method. This is the method which will be used in this research.

[2] Pores across which little or no fluid migration is possible (Bear, 1988).

Chapter 5 Method

The sequential nature of this testing has meant the design of a given mix was often determined by the success or failure of previous mixes. This is the most logical and pragmatic way to conduct these tests, but it requires a lengthy and comprehensive explanation of methods.

Adaptations to the general methods outlined in this chapter are developed in subsequent chapters where appropriate, and results are presented in Chapter 7. This is important, as it documents developments in the understanding of material characteristics and concrete behaviour throughout the course of this research.

5.1 Milling

In order to achieve adequate reactivity and sufficient concrete strength, pumice must be milled to a very fine powder. This is to provide adequate surface area for pozzolanic reactions to occur at an effective rate. Achieving pumice target fineness is critical to this investigation, therefore prior to this thesis, Holcim (NZ) trialled mills across New Zealand, and one in Germany. Trial mills were assessed based on their ability to achieve adequate fineness with acceptable energy consumption. Details of the milling assessment used by Holcim (NZ) are outside the scope of this thesis; but at the end of the selection process, the pumice used was milled at Loesche GmbH, Dusseldorf, Germany.

5.2 Pumice Preparation

A 1.4 tonne pumice sample from Rangiriri was shipped to milling specialist Loesche GmbH. Grinding tests were carried out using the Loesche mill type LM 3.6, a vertical roller mill equipped with two rollers and a top mounted classifier (Figure 5.1). Material is fed directly with a screw conveyor onto a grinding table, where it is taken under rollers for grinding. Ground material is then transported pneumatically to the classifier, and the separated product is conveyed to a hopper where it can be sampled. Air is gas fired to provide the necessary heat for drying (Loesche GmbH, 2011).

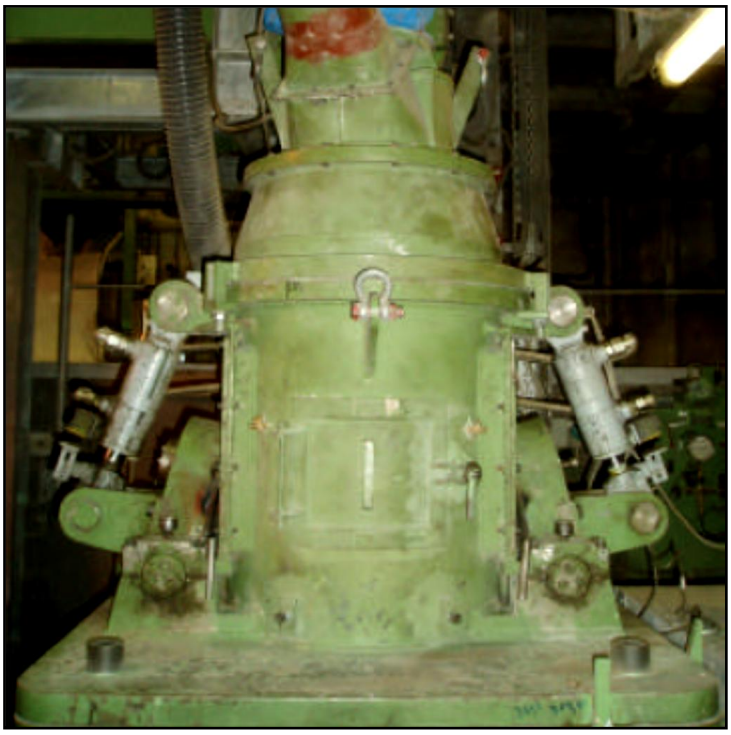


Figure 5.1: Loesche laboratory mill

(Loesche GmbH, 2011)

In the laboratory mill, material must have a moisture content of <6% by mass, and a maximum particle size of 15mm. Therefore, the pumice was dried and crushed before milling. Grinding pressure, grinding table speed, air flow and temperature were held constant, adjusting only the classifier speed throughout the trial. Wear plates were installed on the grinding rollers, and the post-milling mass reduction used to indicate abrasive properties. All operational data was recorded throughout the trial, including power consumption. Specific power consumption (kWh/t) is calculated using the measured torque at the grinding table, the actual grinding table speed, and the shaft of the mill gearbox, with no losses or corrections (Loesche GmbH, 2011).

Pumice was milled in two sub-samples, hereby referred to as Loesche (3k) and Loesche (6k) (according to the protocols of the Loesche facility). Loesche (3k) aimed to match the particle size distribution (PSD) of the milled 'Horotiu pumice', which had been processed in Cement Mill 2 at the Westport Cement Works in 1998 (see Section 3.3). A sample of this was sent to Loesche as a reference.

The second sub-sample targeted a specific surface area (SSA) of 550m^2/kg, based upon pumice used in a similar study by South (2009). These two subsamples were returned to New Zealand, with the following key specifications:

- Loesche (3k) was milled to a SSA of 760 m^2/kg, at a power consumption of 23.2 kWh/t.
- Loesche (6k) was milled to a SSA of 492 m^2/kg, at a power consumption of 8.1 kWh/t.

Although a 1.4 tonne sample was sent to Germany, only 15.8kg of Loesche (3k) and 17.7kg of Loesche (6k) was returned to New Zealand. This constrained the extent of concrete testing which could be undertaken, and required careful management of the available material. Milled pumice SSA and PSD details are provided in Figure 5.2 and Figure 5.3.

5.3 PozzoTech Analysis

An additional pumice sample was sent to the Holcim Support Group (HGRS) and Product Innovation and Support (PIS) in Switzerland, where the material was evaluated according to PozzoTech Working Paper 13 (Holcim, 2003)[1]. Primary objectives included evaluating the chemical composition and mineralogy of the pumice, determining its pozzolanic reactivity, assessing grindability, and concrete/mortar strength performance (Holcim, 2011). Additional pumice samples were tested at the University of Canterbury, and are incorporated in the results (see Section 7.8).

[1] Holcim's standard method for testing and benchmarking globally sourced natural pozzolans.

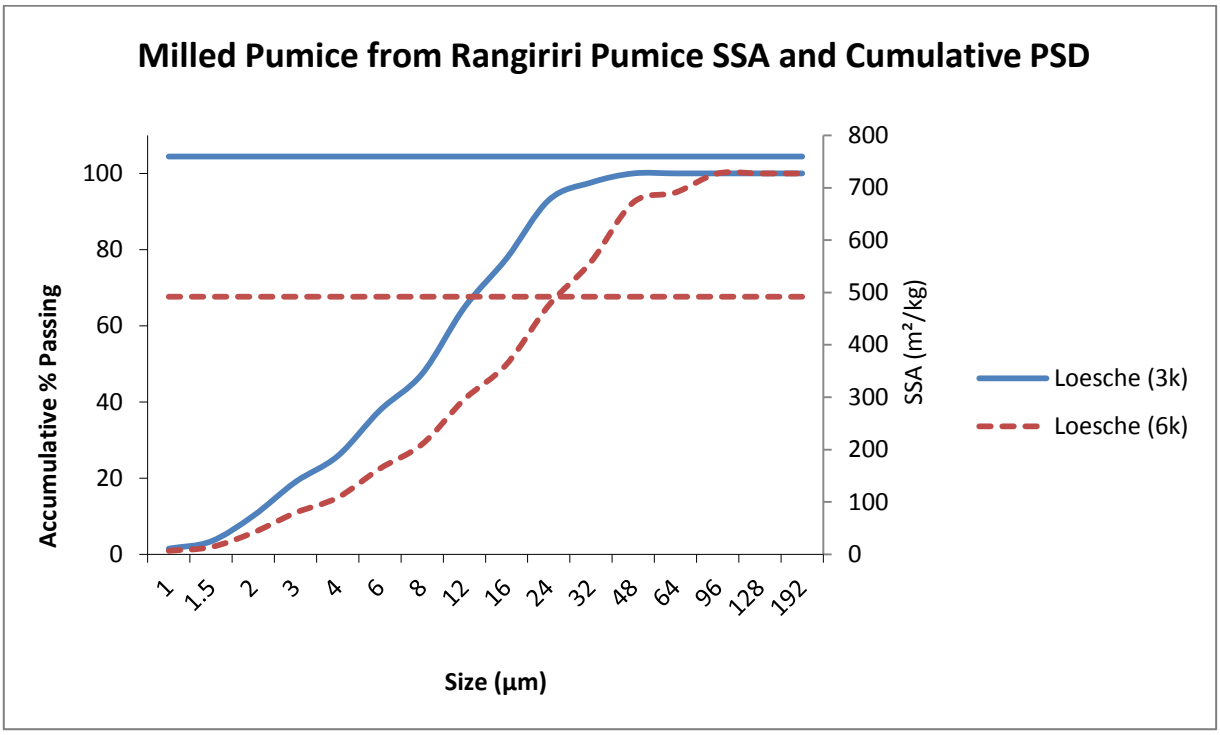


Figure 5.2: Milled pumice SSA and cumulative PSD

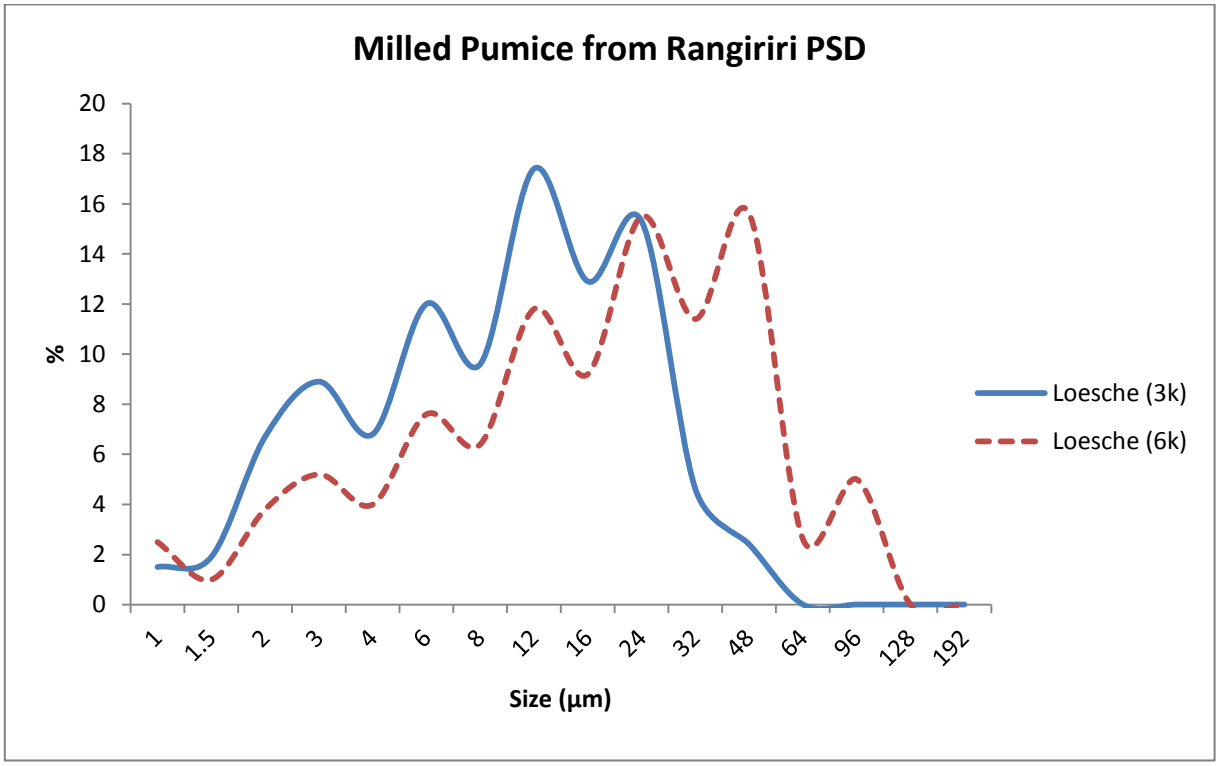


Figure 5.3: Milled pumice PSD

5.4 Scanning Electron Microscopy

To further understand the effects of the milling process, a JEOL JSM6100 Scanning Electron Microscope (SEM) was used to take images of both Loesche milled pumice samples, and the ball milled 'Horotiu pumice'. The primary aim was to identify variations in particle morphology, and how these may affect concrete performance.

SEM images revealed a variety of material shapes, dominated by highly angular particles with a modal size on the order of 5-10µm. Segments of vesicle walls were visible in all samples, and near intact vesicles were observed at all magnifications (eg. Figure 5.4). Tubular vesicles were observed with diameters as small as 1µm diameter (eg. Figure 5.5). Fibrous particles were seen in both Loesche milled Rangiriri samples (Figure 5.6), but not in the Horotiu sample.

Figure 5.7 shows magnified images of the same particle (1500, 5500 and 13000x respectively). These images show the highly fibrous nature of what is believed to be cristobalite. Cristobalite is a high temperature quartz polymorph, and contributes to concrete strength. Cristobalite was also identified in both PozzoTech and University of Canterbury XRD analyses (see Section 7.8.1). Conchoidally fractured particles were noted in each sample, and were possibly small quartz grains[1].

In each sample, small particles appear to have either agglomerated, or undergone additional alteration. These are shown in Figure 5.8 (a typical image of 'Horotiu' pumice morphology) and Figure 5.9. Considering the history of the material, this may be a result of eruptive or sedimentary processes, or the milling process itself. Alternately, as they do not appear to represent typical Taupo Pumice particles, they may be associated with a different eruption altogether. If these particles are in fact agglomerated, an important consideration will be whether these micro-particles are welded or cemented together, or whether they are held by electrostatic (or other) forces. If it is the latter, the addition of superplasticiser may de-flocculate particles, with better dispersion possibly resulting in improved concrete strength.

[1] Further analysis of particle isotropy would refine this. If anisotropic, the particle is probably quartz, and if isotropic, possibly obsidian.

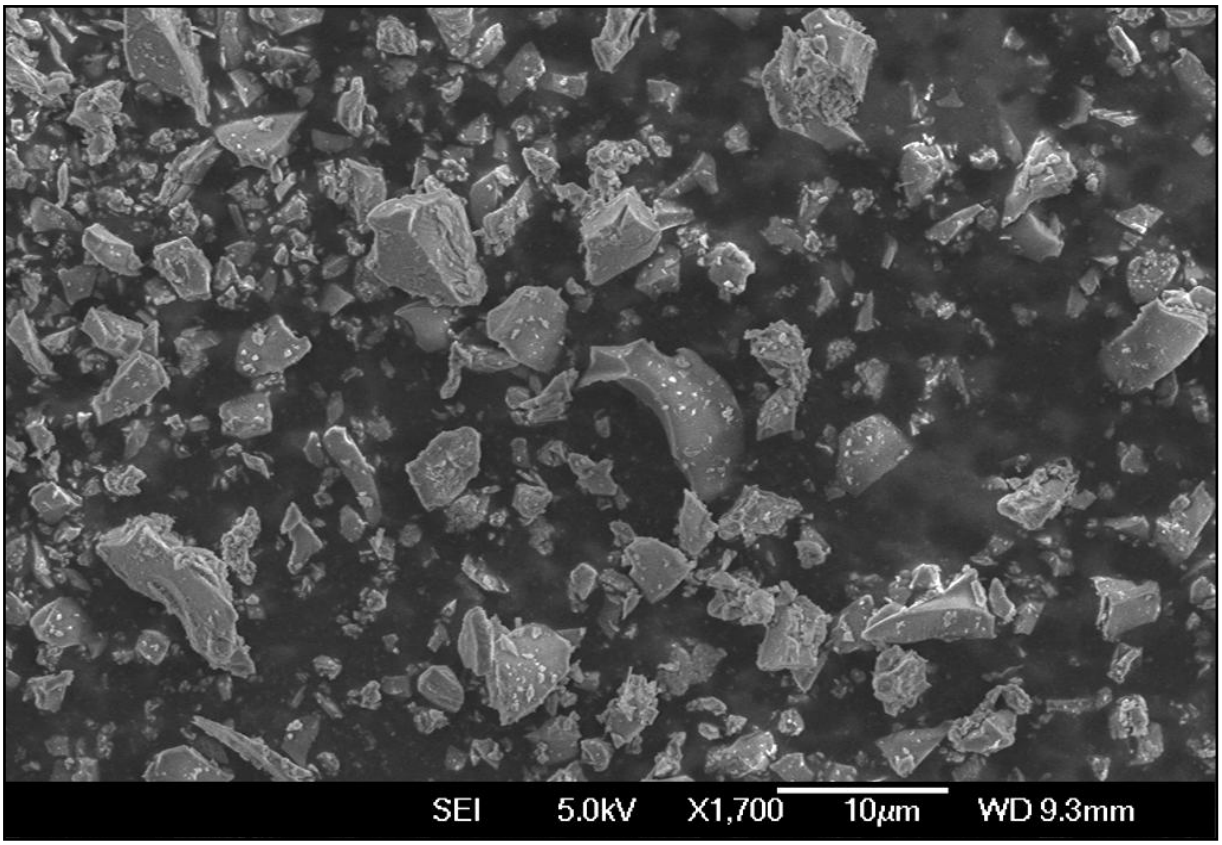


Figure 5.4: SEM Image 1 – Loesche (3k) pumice with partial vesicle walls

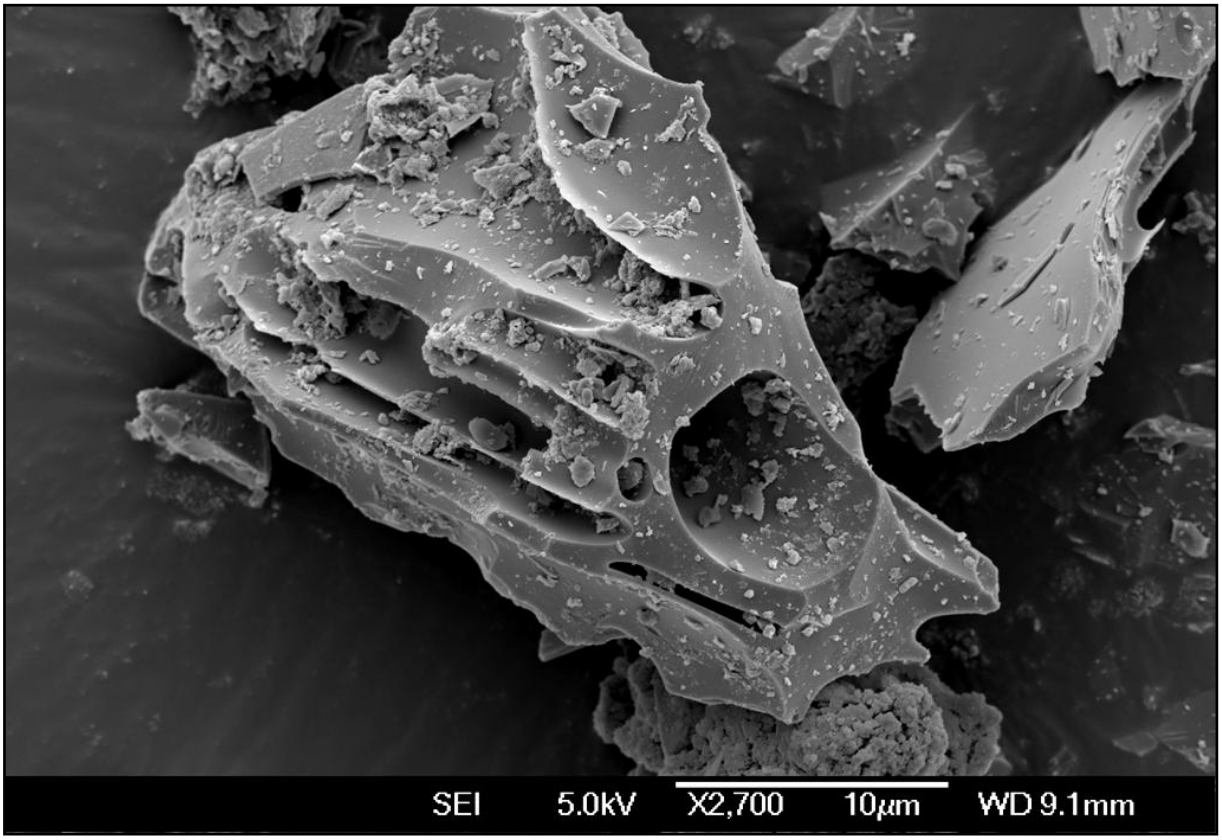


Figure 5.5: SEM Image 2 – Loesche (6k) pumice tubular vesicles

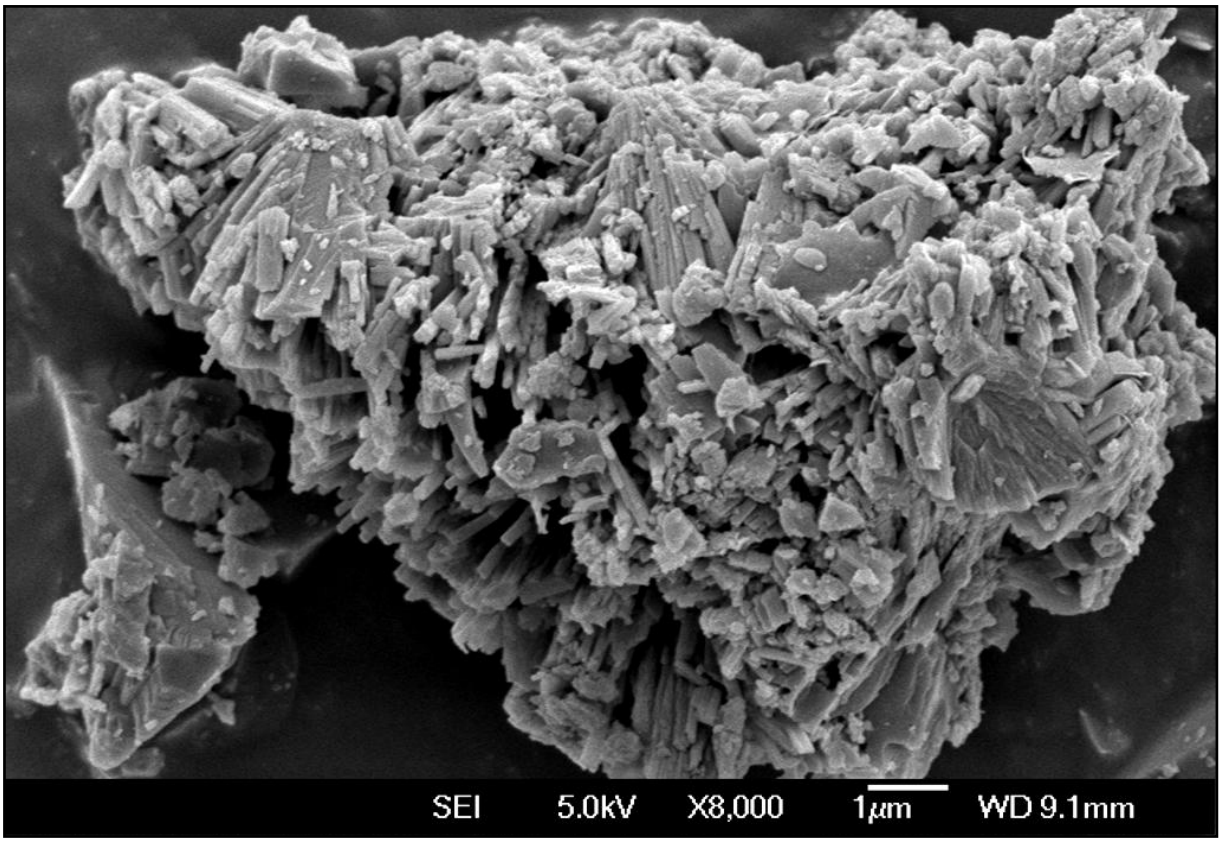


Figure 5.6: SEM Image 3 – Fibrous, agglomerated/altered Loesche (6k) pumice

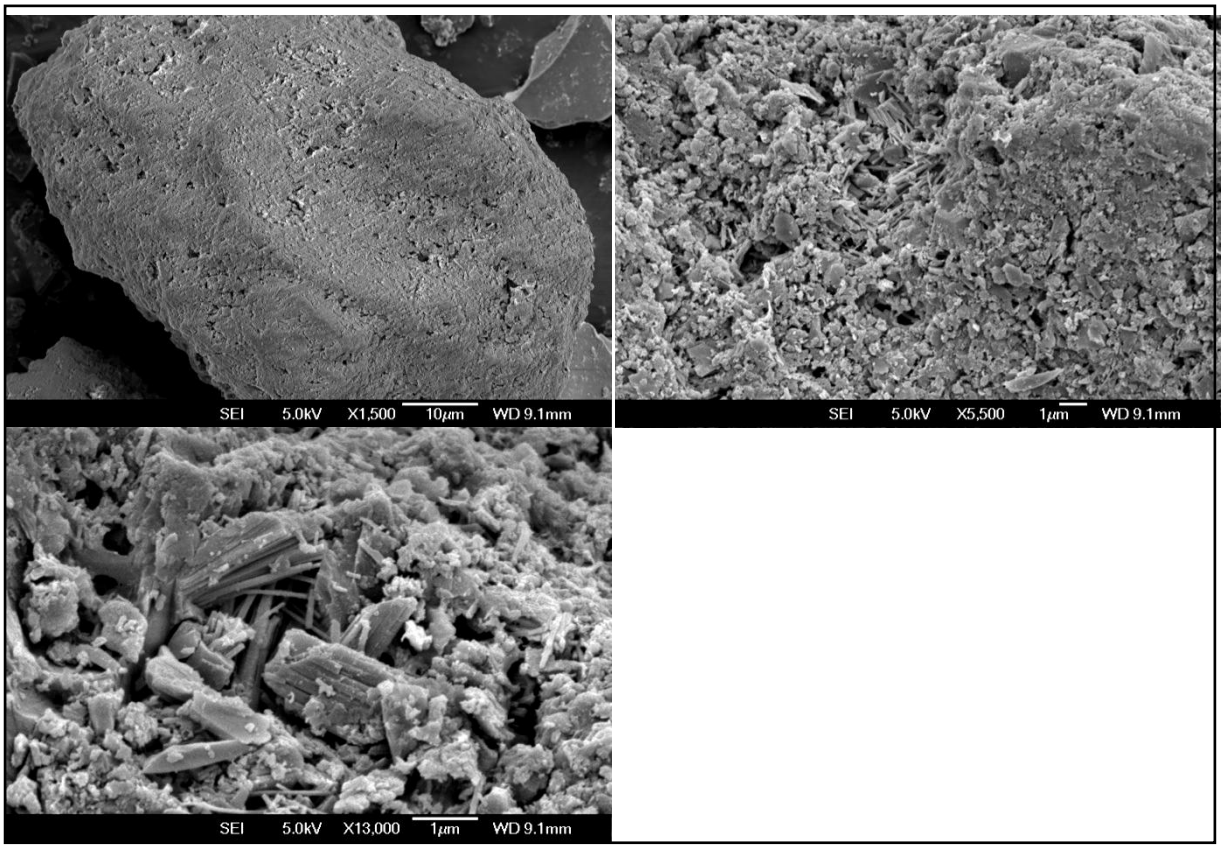


Figure 5.7: SEM Image 4 – Loesche (6k) pumice at increasing magnification

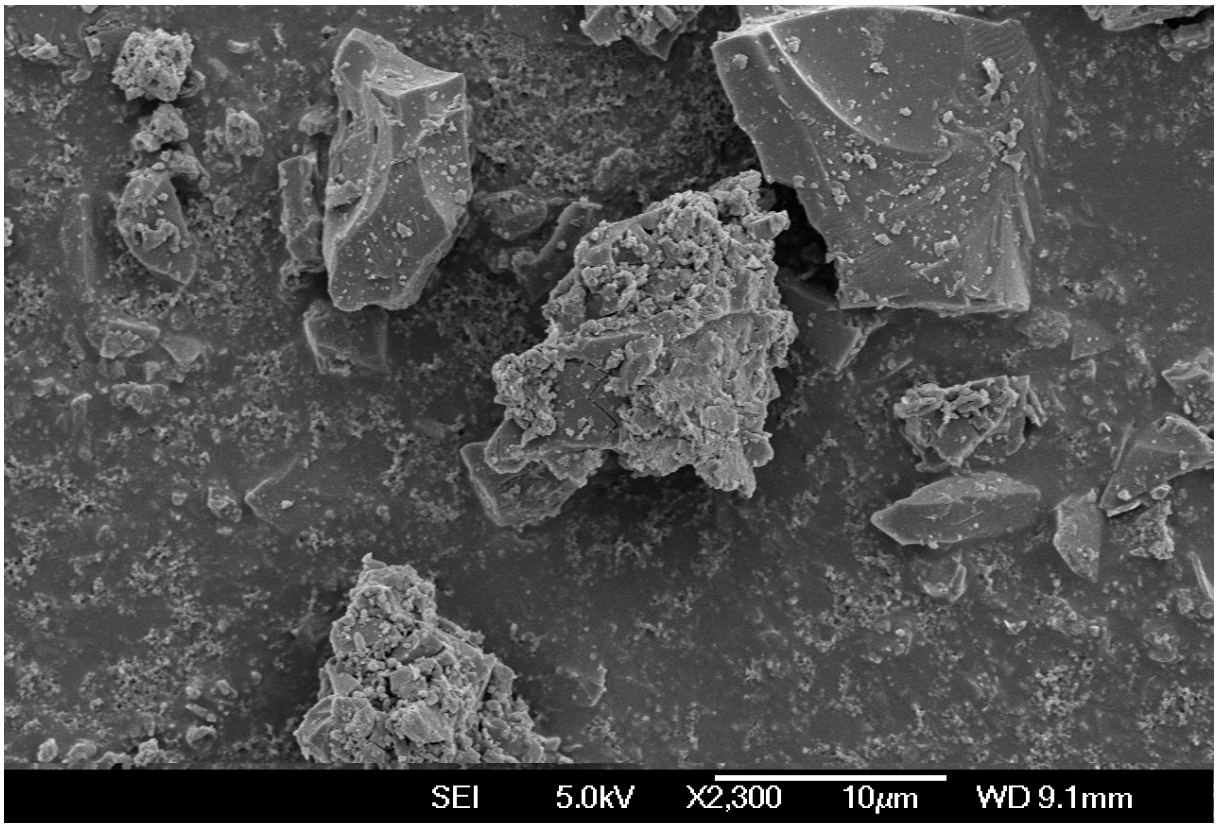


Figure 5.8: SEM Image 6 – 'Horotiu' vesicle walls and agglomerated/altered particles

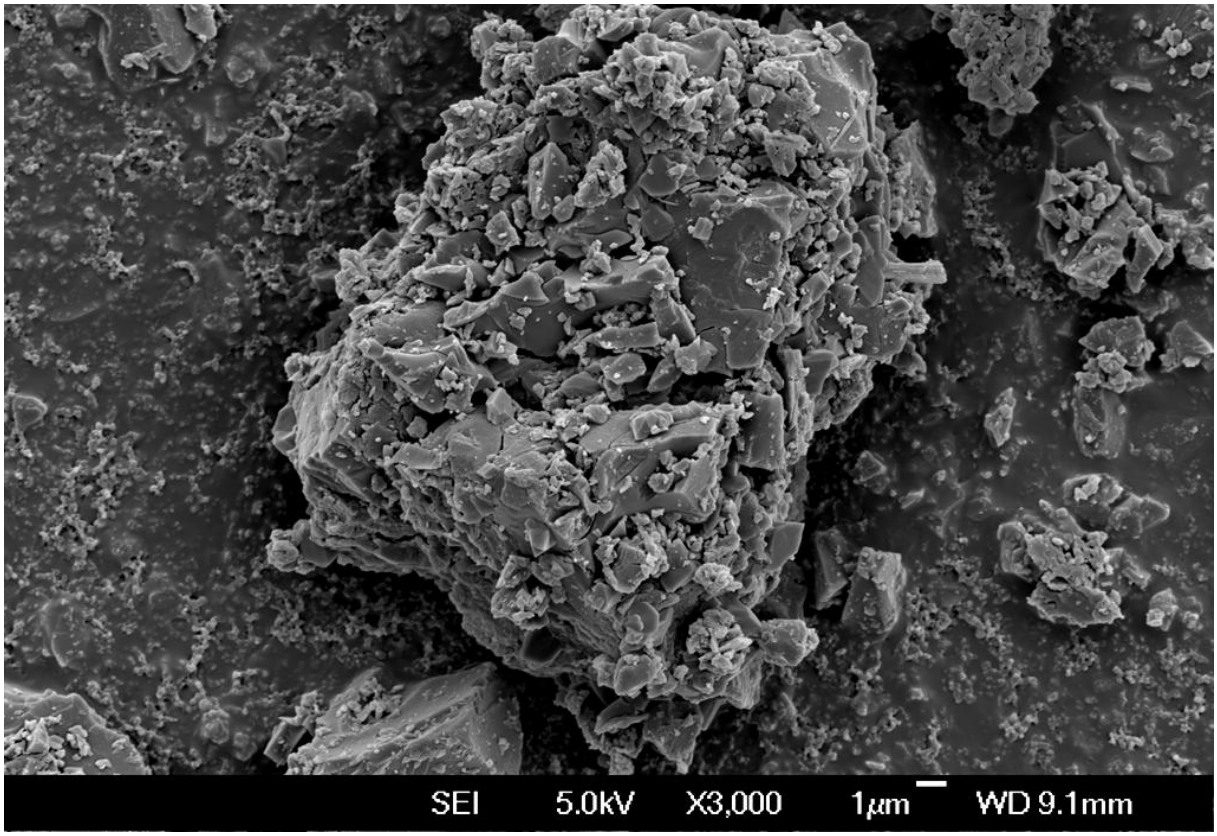


Figure 5.9: SEM Image 5 – Agglomerated/altered 'Horotiu pumice' particles

5.5 Reference Cement

5.5.1 X10-152

The Ultracem reference cement used in Round One of this investigation was an ordinary Portland cement (OPC) type GP Ultracem containing 7.7% limestone and 4.0% gypsum. This cement (X10-152) is a sub-sample of a milling trial conducted at the Westport Cement Works in August 2010. This trial was part of the preliminary investigation process where the Ultracem mineral limestone content was increased from 5% to 10% on a commercial scale.

X10-152 reference concrete showed a reduction in compressive strength in Round One testing (April 2011) compared with the milling trial in August 2010 (Figure 5.10). Variations in strength between the two reference samples are more marked at 3 and 7 days, where the 2011 tests returned 23% and 15% lower compressive strengths respectively. Early age variation may have arisen from the slight hydration of cement during its time in storage, however by 28 days the difference is negligible, and may be attributed to inherent testing variation. X10-152 chemical composition and physical properties are provided in Table 5.1, particle size distribution (PSD) and specific surface area in Figure 5.11.

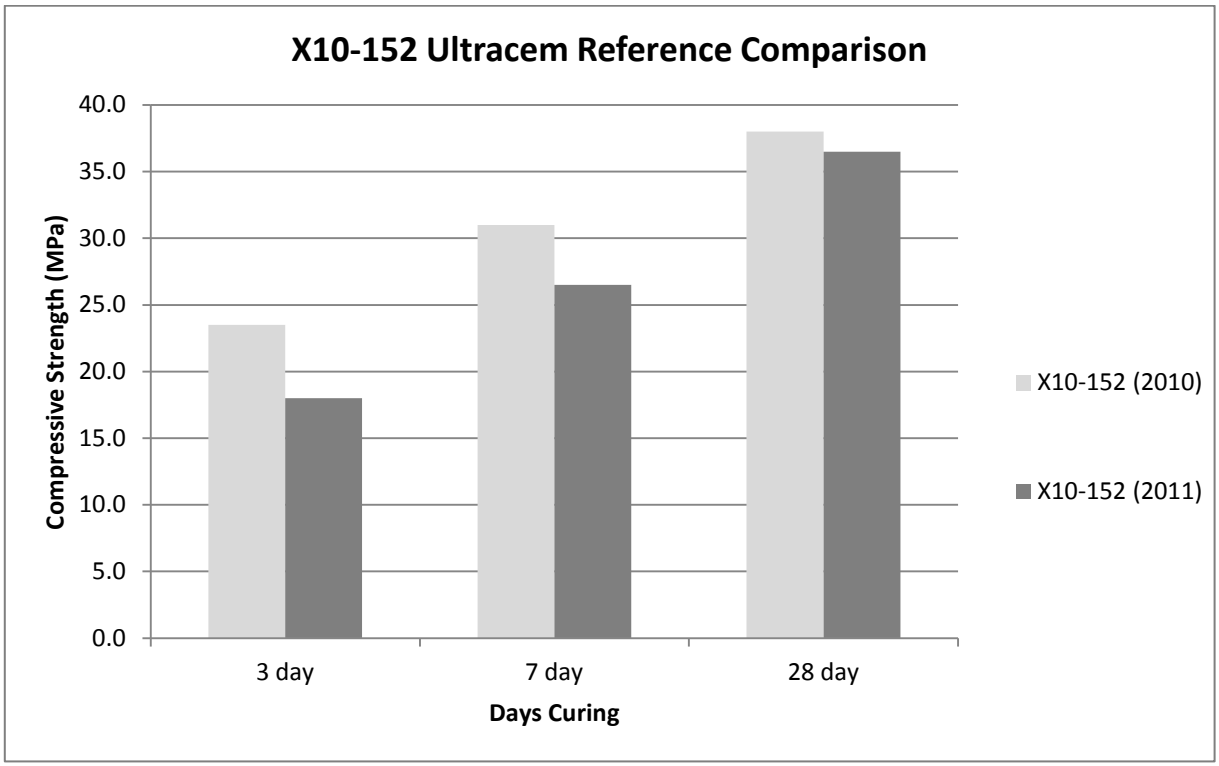


Figure 5.10: X10-152 Ultracem reference comparison

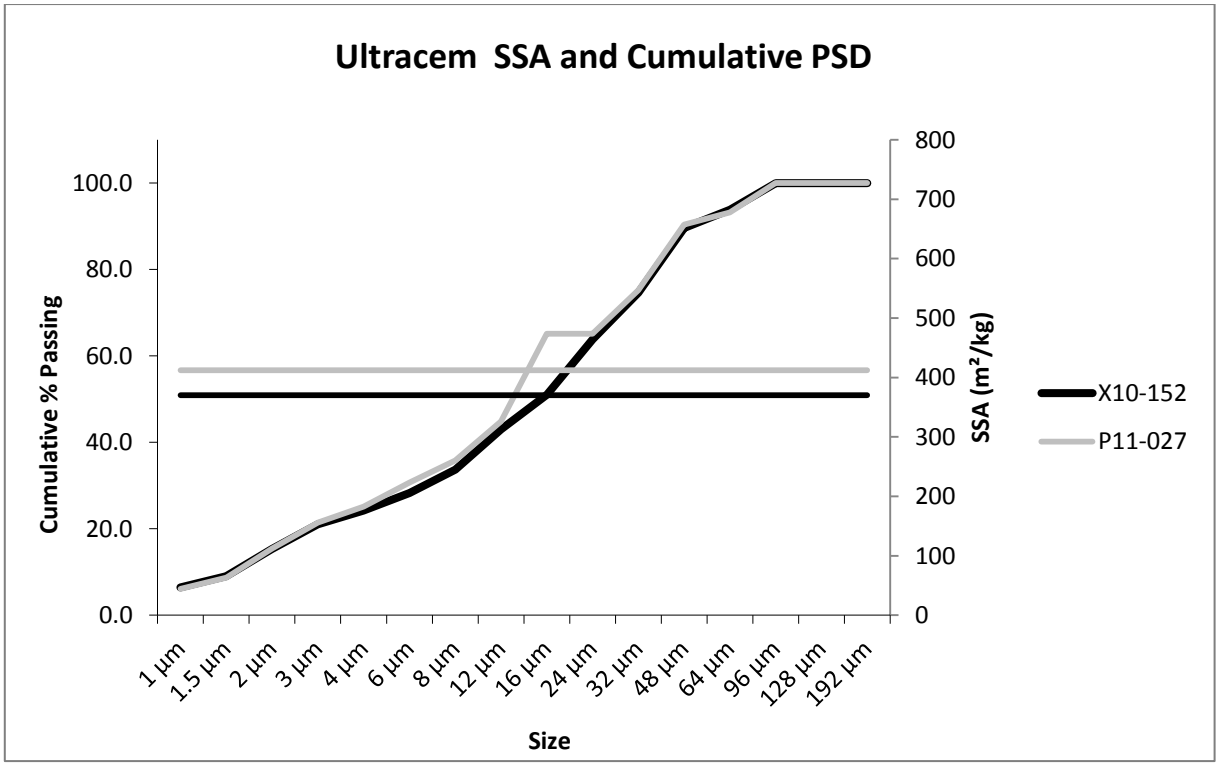


Figure 5.11: Ultracem SSA and cumulative PSD

5.5.2 P11-027

When initial research plans were set in late 2010, the increase in Ultracem mineral limestone content (5% to 10%) had not yet occurred on a commercial scale. However, by the time Round Two concrete testing commenced (having been delayed by the February earthquakes), 10% limestone cement was being produced commercially.

Given the opportunity to use the more modern product, the decision was made to use a new reference cement. The decision was not taken lightly, however as changes to the mix design in the remaining concrete tests already made direct comparisons between the first and subsequent rounds impossible, the benefits were deemed to sufficiently outweigh any negatives.

All remaining concrete testing (Rounds Two, Three and Four) were conducted using the new reference cement (P11-027), which contains 9.35% mineral limestone, reflecting the new commercial product. Properties of this cement are presented in Table 5.1, with cumulative PSD and SSA in Figure 5.11. The two reference cements used are very similar in composition, and have produced similar mortar strengths.

Table 5.1: Reference cement properties

X10-152 Ultracem Properties			
Chemical Properties by XRF (%)		**Mortar Properties**	
CaO	64.01	3 day strength (MPa)	39.0
SiO_2	19.49	7 day strength (MPa)	50.0
Al_2O_3	4.19	28 day strength (MPa)	61.5
Fe_2O_3	2.19		
SO_3	2.70	False set (minutes)	16
MgO	0.74	Initial set (minutes)	105
K_2O	0.60	Final set (minutes)	165
Na_2O	0.12		
Mn_2O_3	0.16	**Sizing**	
TiO_2	0.47	45µm residue (%)	12.60
P_2O_5	0.09	SSA (m^2/kg)	370
Sum	94.67		
Other			
Silica Ratio (SR)	3.06		
Alumina Ratio (AR)	1.91		
Lime Saturation Factor (LSF)	105.02		
LOI (%)	4.19		
NaEq (%)	0.52		
Mineral Limestone (%)	7.7		
P11-027 Ultracem Properties			
Chemical Properties by XRF (%)		**Mortar Properties**	
CaO	63.49	3 day strength (MPa)	41.5
SiO_2	18.91	7 day strength (MPa)	50.5
Al_2O_3	4.24	28 day strength (MPa)	58.5
Fe_2O_3	2.19		
SO_3	3.34	False set (minutes)	18
MgO	0.72	Initial set (minutes)	105
K_2O	0.51	Final set (minutes)	150
Na_2O	0.20		
Mn_2O_3	0.14	**Sizing**	
TiO_2	0.21	45µm residue (%)	12.38
Sum	93.95	SSA (m^2/kg)	412
Other			
Silica Ratio (SR)	2.94		
Alumina Ratio (AR)	1.94		
Lime Saturation Factor (LSF)	106.95		
LOI (%)	5.18		
NaEq (%)	0.54		
Mineral Limestone (%)	9.35		

5.6 Concrete Preparation

As the success of the incorporation of pumice is largely determined by concrete strength, it is important that recognised preparation and testing methods are used. The following procedures are based on NZS 3112: Part 2: 1986 (Tests Relating to the Determination of Strength of Concrete), and further defined in Westport laboratory procedures.

River sand and greywacke aggregate were sourced from Fulton Hogan, Christchurch, using two thirds 19mm and one third 13mm stone. Sand and aggregate PSD's are provided in Appendix 4. After predetermining sand and aggregate moisture content and adjusting the mix water[1] accordingly; aggregate, sand, cement and pumice were added to the concrete mixer in that order. After briefly blending, water reducer or superplasticiser was added to the water (depending on mix design), then added to the concrete mixer. Concrete was mixed for 2.5 minutes, trowelled toward the centre, and mixed for a further 30 seconds.

Slump and air entrainment were measured according to methods specified in NZS 3112 (Figure 5.12). Calcium and sodium lignosulphonates are commonly used as water reducers (Taylor, 1997), and a sodium lignosulphonate (Sika BV50W) used in this research. Water reducers are added to concrete to reduce the amount of water required to achieve target slump, or to improve workability at a fixed water addition. When cement is mixed with water, the system flocculates, causing clusters of solid particles to form. Water reducer acts by breaking up these clusters into almost individual particles (Ramachandran, 1995).

Figure 5.12: Measuring concrete slump

[1] Potable water used in the preparation of fresh concrete.

The cylindrical concrete moulds used were 200mm in length with a 100mm diameter (Figure 5.13). Moulds were filled in approximately thirds. Each third was compacted using 25 strokes with a tamping rod, and the sides of the moulds tapped with a mallet 10 times at two separate points across the circumference. Immediately following compaction, the surface of the cylinder was worked to remove any depressions greater than 1mm using rotary motion with a top plate. Cylinders were then immediately transferred into the curing room, where they were cured at 21± 2ºC. These were left undisturbed for 24 ± 4 hours, after which they were removed from their moulds. Cylinders were labelled and weighed, then returned to the curing room until their respective testing dates.

Figure 5.13: Freshly moulded concrete cylinders

All cylinders were broken using a rubber cap, and each reported concrete strength is the mean of two separate strength tests reported to the nearest 0.5 MPa. This differs from the three tests specified in the New Zealand Standard, although is consistent with standard

procedure in the Westport concrete laboratory, and accepted by IANZ (International Accreditation New Zealand)[2].

5.7 Electrical Resistivity

To test the electrical resistivity of the blended concrete, cylinders were cut into approximately 60mm lengths, and placed in a vacuum chamber for three hours. In a separate chamber, a saturated $Ca(OH)_2$ solution was also placed under vacuum for three hours. The solution was then added to the chamber containing the concrete sections, immersing concrete samples, and placed under vacuum for an additional hour. After this the chamber was opened, and the immersed samples exposed to open air for an additional 18 hours. Each concrete section was then placed between two electrodes, and a 250µA alternating current was applied (Figure 5.14). Voltage and current were measured across the sample, and used to calculate the resistance. Results are presented in Section 7.7.2.

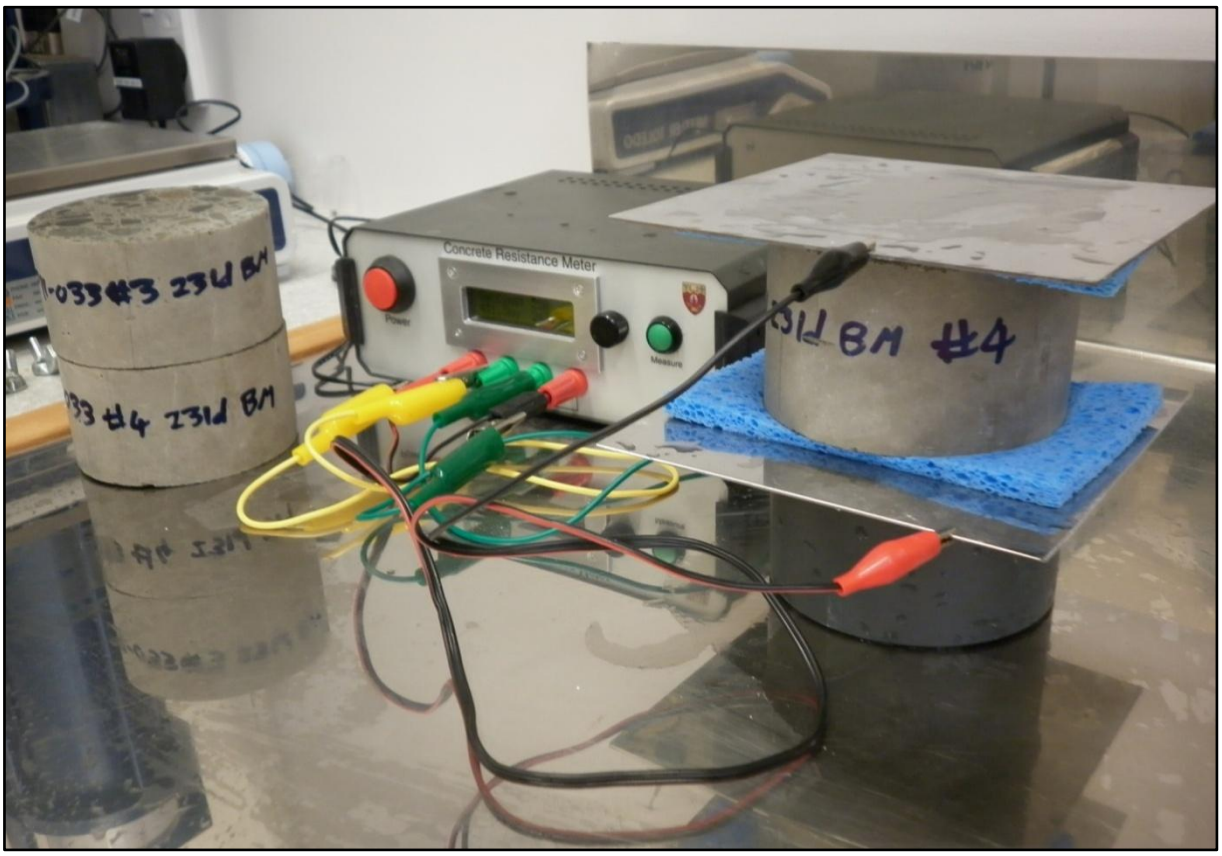


Figure 5.14: Concrete resistance meter

[2] In addition, the number of cylinders cast was partially determined by the availability of milled pumice. The extent of analysis undertaken in this thesis would not have been possible had three cylinders been made per test.

5.8 Bulk Diffusion

Chloride diffusion profiles and coefficients were determined using bulk diffusion, based on methods described in ASTM C1556. 60mm concrete sections were sealed on all except one face using Sikadur 32 epoxy bonding agent. These were vacuum saturated, and immersed in a 2.8M NaCl solution for 35 days. This section was profile ground inward from the exposed face at 2mm increments (Figure 5.15), the acid soluble chloride concentration determined by mixing 4g of sample with 2ml of 0.5N nitric acid and 5ml distilled water, and leaving to rest for at least one hour. Samples were then mixed with 2.5ml of 0.85M sodium acetate, and a further 70ml distilled water. A potentiometric titration with 0.1N silver nitrate was then performed to determine chloride concentration at each depth (Figure 5.16). Results are presented in Section 7.7.3.

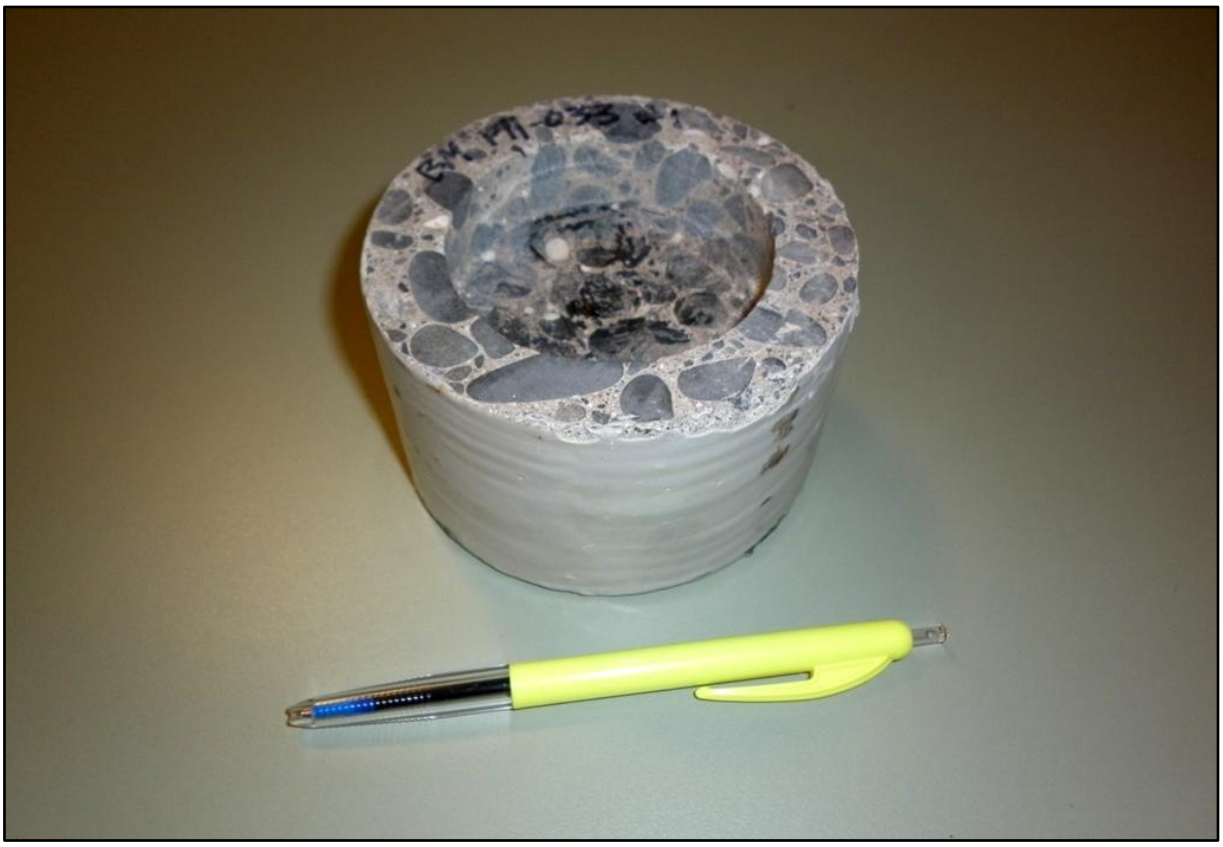


Figure 5.15: Profile ground concrete cylinder

Figure 5.16: Chloride analysis using Metrohm autotitrator

5.9 Porosity

Porosity was determined using methods described in ASTM C642 – 06, placing 25mm concrete sections under vacuum for three hours, and placing water under vacuum for one hour. Samples were then immersed in the water, and exposed to the open air for 18 hours. Following this exposure period, samples were towelled dry and weighed, and weighed while submerged. These values were used to calculate the volume of permeable pore spaces, expressed as a percentage of total volume. Results are presented in Section 7.7.1.

Chapter 6 Concrete Mix Designs

As previously mentioned, the availability of milled pumice controlled the range and extent of concrete tests which could be undertaken for this thesis. Through careful planning and management, enough pumice was available for the necessary tests. The testing schedule was designed to produce the most meaningful results with minimal waste. Concrete strength testing was divided into four rounds, and durability testing was conducted using the Round Two mix design.

6.1 Round One

Round One concrete was made using the same mix design used in routine Holcim Ultracem testing at the Westport Cement Works, allowing direct comparison. These methods are based on standards specified by NZS 3112 (Specification for Methods of Test for Concrete) (see Section 5.6), and were used to create a robust baseline dataset.

The Ultracem reference concrete was mixed to a fixed water/cement ratio of 0.6 (see Section 5.5). SIKA BV50W water reducer was added at 455ml/100kg binder. The baseline dataset was established by replacing cement with each of the milled pumice samples at 5, 10, 15 and 30% by mass. All other variables were held constant. Details of the nine Round One mixes are presented in Table 6.1, with additional concrete properties in Appendix 5.

6.2 Round Two

Although Round One compressive strengths were below Ultracem reference levels in all tests up to 28 days, a useful baseline dataset was created. The object of Round Two testing was therefore to improve on Round One concrete strengths by reviewing and adjusting the mix design.

Achieving a higher nominal strength alone (by reducing w/b ratio) is not useful from a commercial or research perspective. Rather, if the mix adjustment is to provide meaningful outcomes, it must not only achieve higher nominal strengths, but gain strength relative to an appropriate Ultracem reference.

Comparisons were made between the Holcim standard 30MPa Ultracem mix design (Round One), and designs used in similar research by South (2009) and Brown (1998). Examination of the Round One design revealed that the mix was substantially oversupplied with sand, and not representative of what would be commercially produced at a concrete batching plant. Although sand is essentially inert in the concrete mix, significant oversupply may actually influence concrete strength and workability. Replacing cement with pumice by mass actually results in a greater volume of pumice being added (SG=2.642) than the cement it replaces (SG=3.110). It was therefore decided that desired concrete yield would be maintained by adjusting sand content with respect to the pumice addition.

To improve concrete performance, a number of changes can be made. Reducing the water content and holding binder constant is desirable from a commercial perspective; but may affect consistency and workability at lower w/b ratios. To assess this, a slump trial was conducted using the more plentiful milled 'Horotiu pumice' at lower w/b ratios. These results were then applied to the Round Two mix design. Five mixes were trialled, adjusting the binder and water content to reduce the w/b ratio to 0.5. Based on these tests, the Round Two mix water was reduced from 173 to 155L/m^3, and binder increased from 289 to 310kg/m^3.

With a higher proportion of binder in the mix, it was hoped that the hydration rate of both the cement and the pozzolan would increase, improving both nominal and relative strength gains. This was the primary method of improving relative strength in Round Two. Adequate slump must also be retained to ensure a workable mix, however for purposes of this investigation, workability requirements were restricted to a laboratory setting only.

Using a w/b ratio of 0.5, the Round Two reference mix (P11-027) had a higher water demand than the Round One reference (X10-152), which was managed by adding extra water reducer as necessary. Each Round Two mix was prepared by initially adding water reducer at 455ml/100kg binder (as per the Round One mix design), adding more as necessary to achieve an adequately workable mix. Round Two mix designs are provided in Table 6.2, with additional concrete properties in Appendix 5.

Table 6.1: Round One concrete mix designs

Round One Concrete Mix Designs									
Pumice ID		Loesche (3k)				Loesche (6k)			
Sample Code	X10-152	P11-018	P11-019	P11-020	P11-021	P11-022	P11-023	P11-024	P11-025
Pumice Addition	0%	5%	10%	15%	30%	5%	10%	15%	30%
Total Binder (kg)	289	289	289	289	289	289	289	289	289
Cement (kg)	289.0	275.0	260.0	246.0	203.0	275.0	260.0	246.0	203.0
Pumice (kg)	0.0	14.0	29.0	43.0	87.0	14.0	29.0	43.0	87.0
Aggregate (kg)	1095	1095	1095	1095	1095	1095	1095	1095	1095
Sand (kg)	960	960	960	960	960	960	960	960	960
Total Water (kg)	173	173	173	173	173	173	173	173	173
WR (kg)	1.534	1.534	1.534	1.534	1.534	1.534	1.534	1.534	1.534
Total (kg)	**2518**	**2518**	**2518**	**2518**	**2518**	**2518**	**2518**	**2518**	**2518**
WR ml/100kg binder	454	454	454	454	454	454	454	454	454

Table 6.2: Round Two concrete mix designs

Round Two Concrete Mix Designs									
Pumice ID		Loesche (3k)				Loesche (6k)			
Sample Code	P11-027	P11-028	P11-029	P11-030	P11-031	P11-032	P11-033	P11-034	P11-035
Pumice Addition	0%	5%	10%	15%	30%	5%	10%	15%	30%
Total Binder (kg)	310	310	310	310	310	310	310	310	310
Cement (kg)	310	294.5	279.0	263.5	217.0	294.5	279.0	263.5	217.0
Pumice (kg)	0	15.5	31.0	46.5	93.0	15.5	31.0	46.5	93.0
Aggregate (kg)	1095	1095	1095	1095	1095	1095	1095	1095	1095
Sand (kg)	877	873	870	866	856	873	870	866	856
Total Water (kg)	155	155	155	155	155	155	155	155	155
WR (kg)	2.500	1.650	2.515	3.373	3.360	2.250	2.790	3.410	3.325
Total (kg)	**2440**	**2435**	**2433**	**2429**	**2419**	**2435**	**2433**	**2429**	**2419**
WR ml/100kg binder	690	456	695	932	928	621	771	942	918

6.3 Round Three

As a thorough baseline dataset had been created in Rounds One and Two, the decision was made to better utilise the remaining milled pumice by focussing on one addition rate, assessing concrete performance under a range of conditions. Therefore, Round Three and Four pumice replacement levels were held constant at 10%. Several mix variations were considered, again focussed on improving concrete strength, particularly at 28 days. To assess the most suitable variations, a number of factors were taken into account.

6.4 Testing Options

6.4.1 Improving Pozzolanic Activity

A study by Shi & Day (2001) compared three methods (mechanical, thermal and chemical) of improving pozzolanic reactivity. The first involved prolonged grinding of the natural pozzolan, the second involved elevated temperature curing, the third involved the addition of chemical activators (Table 6.3). As shown in Figure 6.1, substantial improvements in strength were recorded with the use of the chemical and mechanical methods; however the thermal method actually resulted in a significant decrease at all ages. The most significant increase in 28 day strength was recorded with the addition of 4% $CaCl_2.H_2O$ (Batch C).

Chemical activation was identified as the most economic of the three studied methods, where despite the increased cost per cubic metre of concrete, the marginal cost per unit of strength decreased, and minimal additional plant or machinery was required (Shi & Day, 2001).

Table 6.3: Pozzolan activation methods (Shi & Day, 2001)

Batch	Activator	Curing Temperature (°C)	Pozzolan SSA (m^2/kg)	Activation Method
A	None	50	291	Control
B	4% Na_2SO_4*	50	291	Chemical
C	4% $CaCl.2H_2O$*	50	291	Chemical
D	None	23	291	Thermal
E	None	65	291	Thermal
F	None	50	385	Mechanical
G	None	50	554	Mechanical
*Based on mass of lime-pozzolan blends				

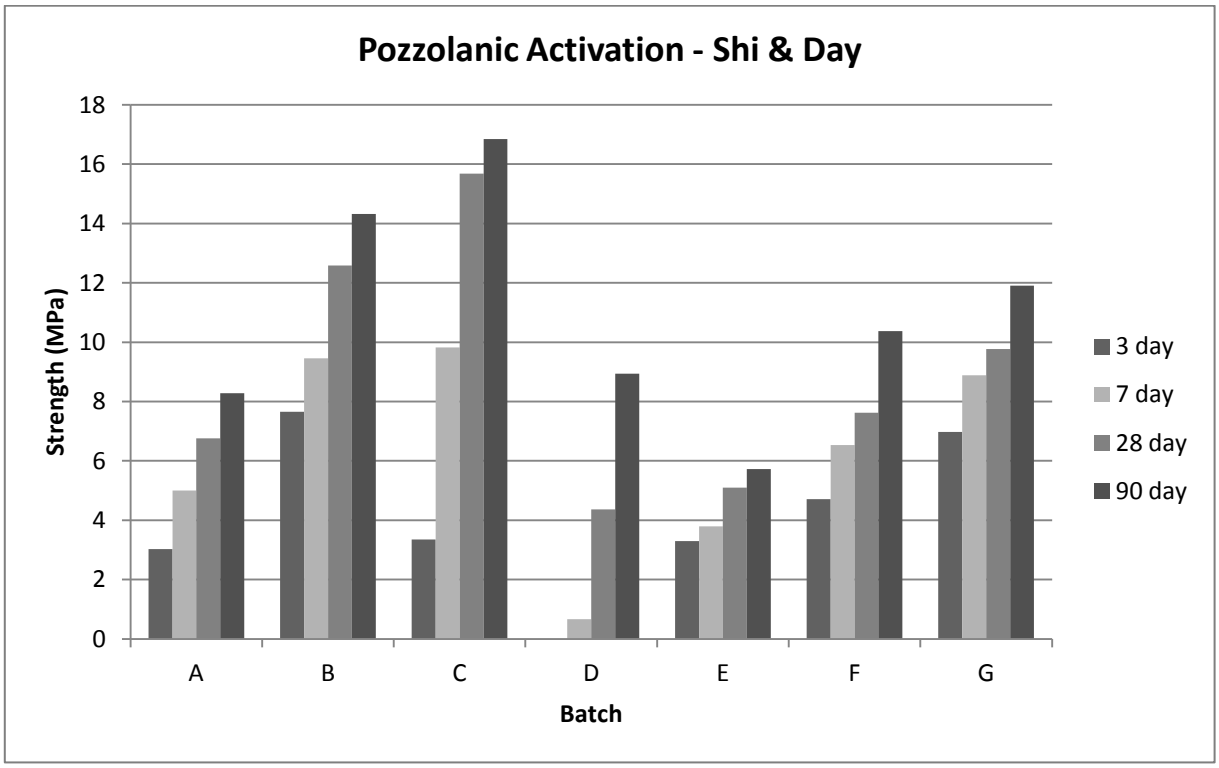


Figure 6.1: Pozzolan activation compressive strength
*See Table 6.3
(Shi & Day, 2001)

6.4.2 Concrete Solution pH

Following the theme of chemical activation, consideration was given to the affect on the mix pH with the addition of milled pumice. If the pumice was acidic, pozzolanic activity may be suppressed at early ages by the liberation of H^+ ions, lowering the pH and inhibiting hydration. This could then improve at later ages as the concrete pH gradually increases with the liberation of OH^-.

To test this idea, 5g of cement was mixed with 200ml of distilled water, with the solution pH measured at 0, 1.5, 3 and 24 hours. The experiment was repeated replacing cement with 10, 30 and 100% pumice, 100% high grade limestone (HGL), and 100% cement kiln dust (CKD), allowing the effects to be compared across a range of available materials.

pH results are presented in Figure 6.2, where it can be seen that the pumice solution is basic, effectively ruling out significant contamination with H^+ ions. Here, it can also be seen that the pH of the 100% pumice sample is an order of magnitude below Ultracem at 24 hours.

While the addition of 10 and 30% pumice result in only slight reductions in pH, these may still contribute to the reduction in early concrete strength.

Although this test disproved the initial idea, it provoked thought into the availability of OH^- ions in the concrete mix. It was considered whether increasing pH and the availability of OH^- at early stages of curing could improve early concrete strength. This could compensate for the reduction in solution pH caused by the pumice.

Bondar et al., (2011) tested the use of chemical activators on pozzolan blended cements in an attempt to improve early strength development. In this study, it was found that geopolymer binders could be synthesised by activating natural pozzolans, condensing them with sodium silicate in a highly alkaline environment[1]. The high alkali content causes aluminium and silicon ions to dissolve, forming a geopolymer paste (Bondar, et al., 2011).

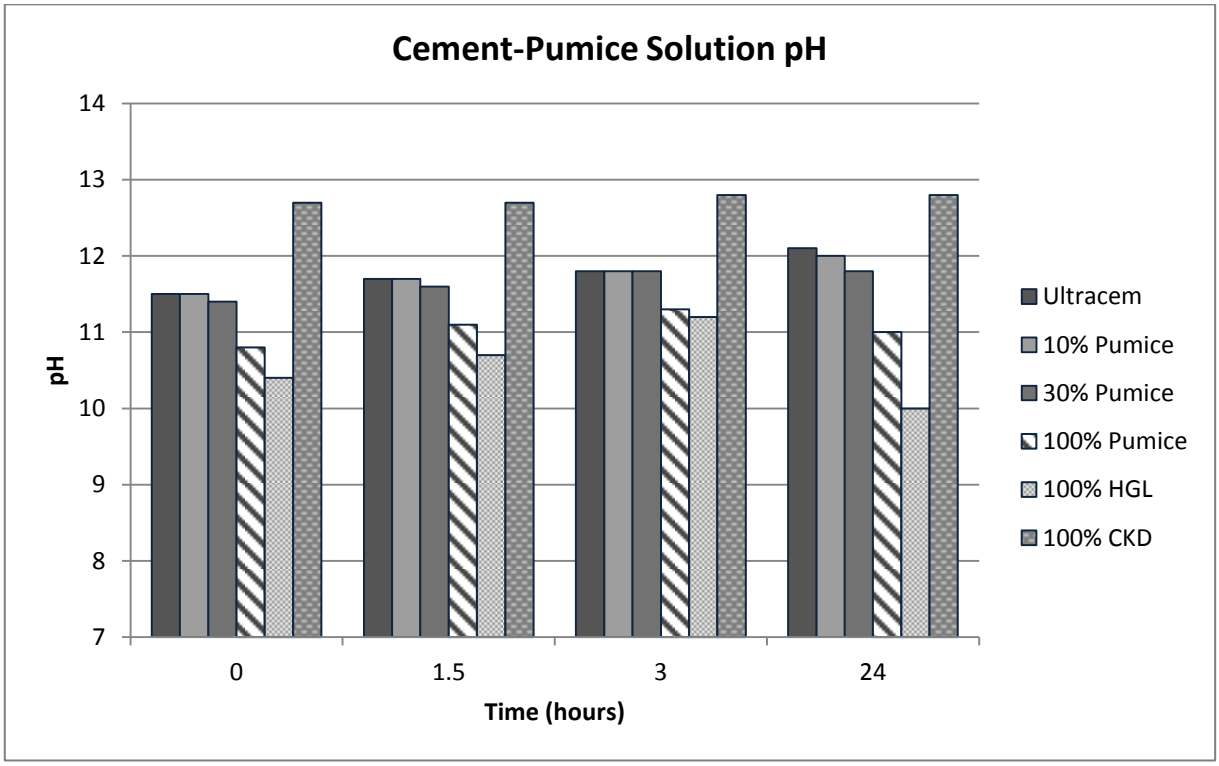


Figure 6.2: Pozzolan solution pH

[1] In this paper, the term 'geopolymer' was used to describe a family of mineral binders which have a polymeric silicon-oxygen-aluminium framework, requiring reactive precursor materials and high concentrations of OH^- (Bondar, et al., 2011).

6.4.3 Pumice Micro-Porosity

Consideration was also given to pumice micro-porosity, and whether its ability to adsorb mix water could affect w/b ratio and/or cement hydration. SEM images show that this pumice is still porous, even when milled very finely (eg. Figure 5.5). Therefore, pumice will likely adsorb mix water immediately upon wetting, effectively reducing the amount of free water for an unknown period of time.

While a reduction in effective w/b ratio will increase concrete strength, stoichiometric principles show that for complete cement hydration, the minimum w/c ratio is between 0.38-0.42 (Neville, 2006; Taylor, 1997)[2]. Therefore, if enough water was absorbed, concrete hydration could actually be impeded.

To test this idea, basic pumice absorption properties were considered. Laboratory tests showed that fresh Taupo pumice from Rangiriri is capable of holding up to 40% moisture without reaching saturation. Assuming milled pumice can also adsorb 40% moisture (which would require verification), at w/b=0.5, a 10% pumice addition could temporarily 'remove' up to 12.4L of water from a $1m^3$ mix, 30% pumice removing $37.2L^3$. If the above quantities of water were removed, w/b ratio could reduce from 0.5 to an effective ratio of 0.46 and 0.38 respectively.

Reducing the w/b ratio to levels above the minimum requirement should increase strength, however this was not observed in Round One or Two. This may suggest two things. Firstly, milled pumice may not actually absorb any substantial quantity of water, leaving the w/b ratio unchanged. Alternately, the addition of milled pumice, which in itself is slow to react, may actively impede the hydration of the remaining cement through another mechanism. While strength development was impeded with the addition of pumice, it is unlikely that hydration is suppressed due to a lack of water with 10% pumice. At 30% replacement, this may be possible, although further investigation would be required to assess absorption properties, and how long (if at all) this water was effectively unavailable.

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[2] This may vary when cement is partially replaced with pumice.

[3] Based on the Round Two mix design.

6.5 Round Three

Overall results from the tests and literature reviews were incorporated into the testing regime for Rounds Three and Four. Round Three tested the effect of high pH mix water on blended concrete strength, where the pH was increased from 7.5 to 12.9 by adding cement kiln dust (CKD)[4].

CKD was added to the mix water, which was vacuum filtered after 30 minutes to remove solids, and subsequently used in the concrete mix. Concrete was made with 10% additions of both pumice samples, and a reference high pH mix. When water reducer was added to the high pH water, a colour change was observed, and it was less effective. Higher doses were required to achieve adequate slump in each of the two pumice-cement mixes. Mix designs are provided in Table 6.4, and additional concrete properties in Appendix 6.

Table 6.4: Round Three concrete mix designs

Round Three Concrete Mix Designs			
	High pH Reference	**10% 3k + High pH**	**10% 6k + High pH**
Sample ID	P11-046	P11-047	P11-048
Pumice Addition	0%	10%	10%
Total Binder (kg)	310	310	310
Cement (kg)	310	279	279
Pumice (kg)	0	31	31
Aggregate (kg)	1095	1095	1095
Sand (kg)	875	868	868
Total Water (kg)	155	155	155
WR (kg)	2.500	3.500	3.845
Total (kg)	**2438**	**2432**	**2432**
WR ml/100kg binder	690	967	1062

6.6 Round Four

Improving the dispersion of cement and pumice particles using superplasticiser (SP) was explored as a way to improve concrete strength. SP improves the fluidity of concrete by dispersing cement particles in the paste. SP is available in several types, including formaldehyde condenses of β-naphthalene sulphate, which disperse cement particles by electrostatic repulsion. Polycarboxylic acids are another type, which disperse particles using

[4] A highly alkaline by-product of the cement manufacturing process at the Westport plant.

steric hindrance[5] (Yoshioka, et al., 2002). Superplasticisers are easily obtained in New Zealand, and are commonly used in a variety of concrete applications.

To test the effect of superplasticiser (SP) on blended concrete strength development, seven mixes were made using Sika ViscoCrete 5-555, a polycarboxylate SP. The first batch used SP at 144ml/100kg binder (as per the manufacturer's guidelines) and no pumice, establishing an SP reference mix. This SP addition was then used in the Loesche (3k) baseline mix, although significantly more was required to achieve a workable mix with the Loesche (6k) pumice. Each mix was repeated using 80% and 120% of the respective baseline SP addition (Table 6.5). Mixes were labelled using SP (1) to denote the baseline, and SP (0.8) and (1.2) to denote the relevant variations. All concretes were made at w/b=0.5, and further concrete properties are presented in Appendix 6.

Table 6.5: Round Four concrete mix designs

Round Four Concrete Mix Designs							
	SP Reference	**10% 3k + SP (1)**	**10% 6k + SP (1)**	**10% 3k + SP (0.8)**	**10% 6k + SP (0.8)**	**10% 3k + SP (1.2)**	**10% 6k + SP (1.2)**
Sample ID	P11-049	P11-050	P11-051	P11-052	P11-053	P11-054	P11-055
Pumice Addition	0%	10%	10%	10%	10%	10%	10%
Total Binder (kg)	310	310	310	310	310	310	310
Cement (kg)	310	279	279	279	279	279	279
Pumice (kg)	0	31	31	31	31	31	31
Aggregate (kg)	1095	1095	1095	1095	1095	1095	1095
Sand (kg)	881	872	872	873	873	873	872
Total Water (kg)	155	155	155	155	155	155	155
SP (kg)	0.492	0.492	0.925	0.392	0.740	0.590	1.107
Total (kg)	**2441**	**2432**	**2433**	**2433**	**2434**	**2434**	**2433**
SP ml/100kg binder	144	144	271	115	217	173	325

[5] Steric hindrance is the mechanical prevention of two particles agglomerating, where particles are uniformly coated in a non-polar organic compound (Shanefield, 1999).

Chapter 7 Results and Discussion

To assess and compare concrete performance, the compressive strength results of each round are presented, followed by more detailed analysis of each pumice addition rate, and the effect of pumice fineness. Rounds One and Two are discussed first, assessing baseline blended concrete data.

7.1 Round One and Two Concrete Strength

Round One concrete strengths are presented in Figure 7.1 and Figure 7.2. All mixes have returned strengths below Ultracem up to and including 28 days, although several have shown improvements by 91 days. Round Two concrete strengths are presented in Figure 7.3 and Figure 7.4, where strengths are again below Ultracem at up to 28 days. These have generally not performed as well as Round One at 91 days, where most strengths are still below Ultracem. Ultracem strength development has essentially ceased by 28 days in Round One, and significantly slowed in Round Two. All blended mixes continue to trend upward at 91 days, suggesting that strength development continues beyond this age. Concrete strengths are presented with respect to curing time in Appendix 7 and Appendix 8.

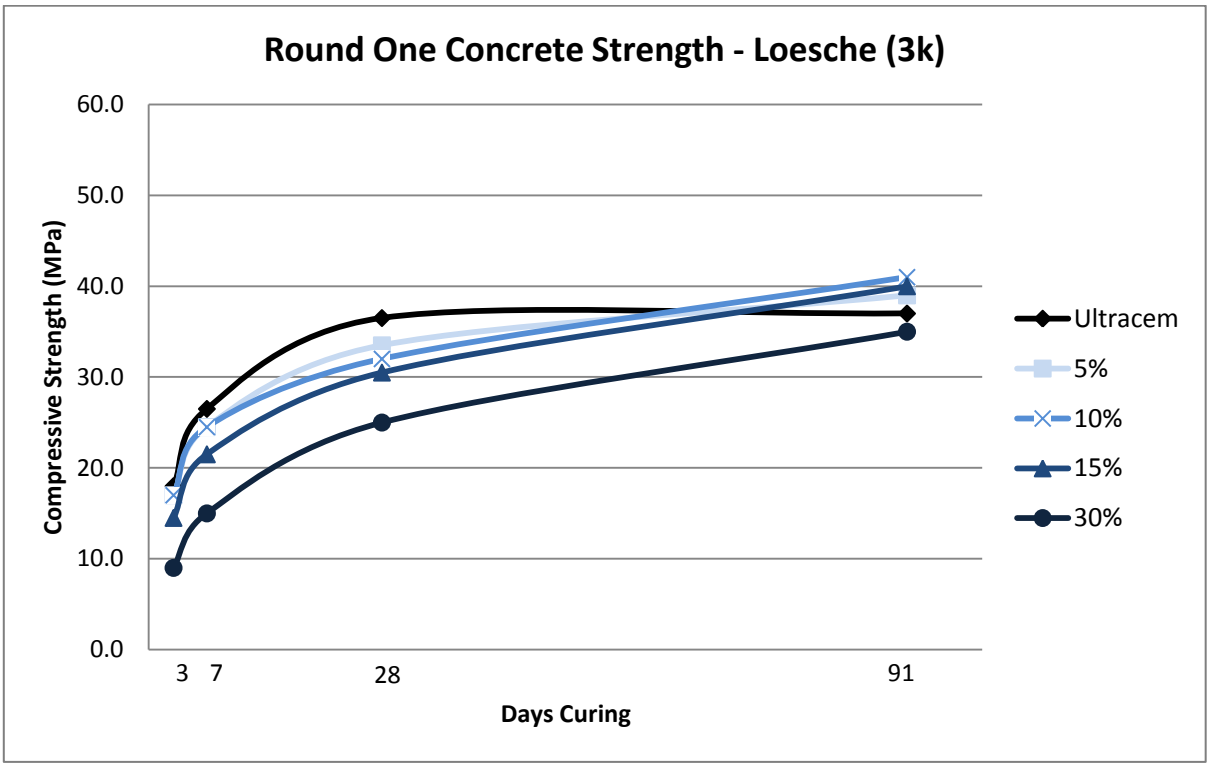

Figure 7.1: Round One concrete strength – Loesche (3k)

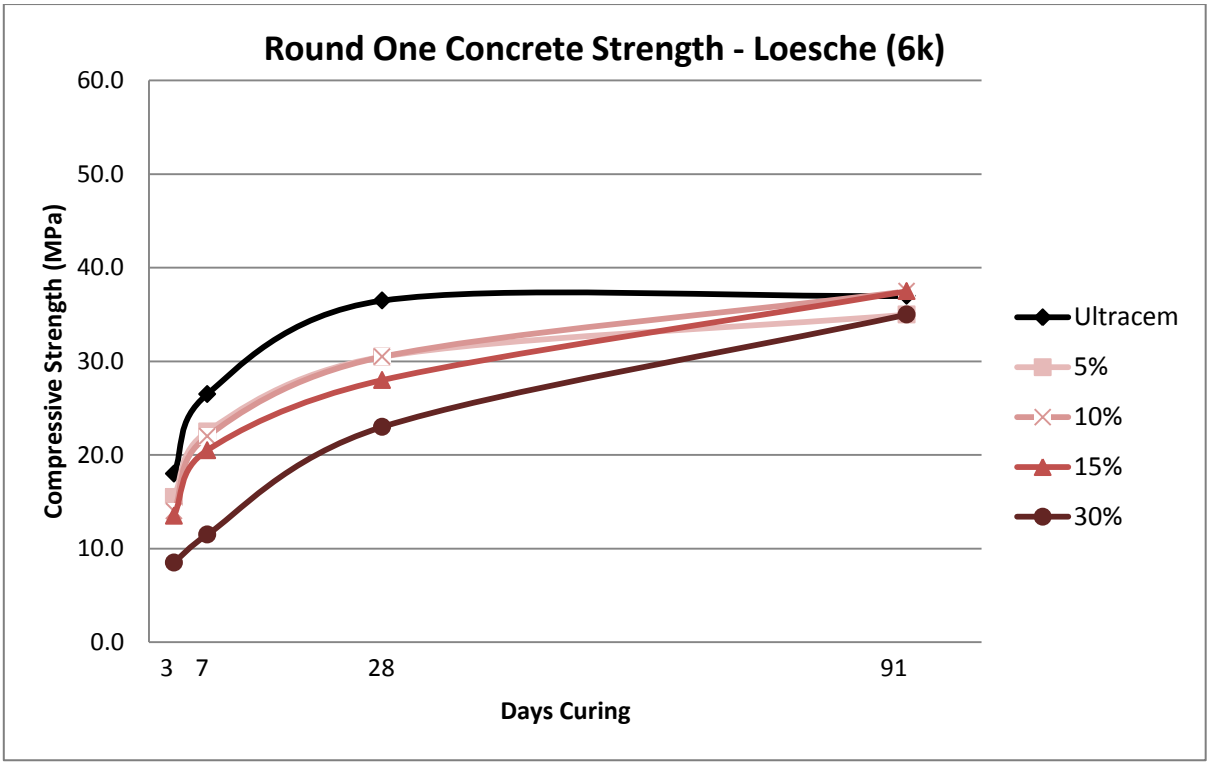

Figure 7.2: Round One concrete strength – Loesche (6k)

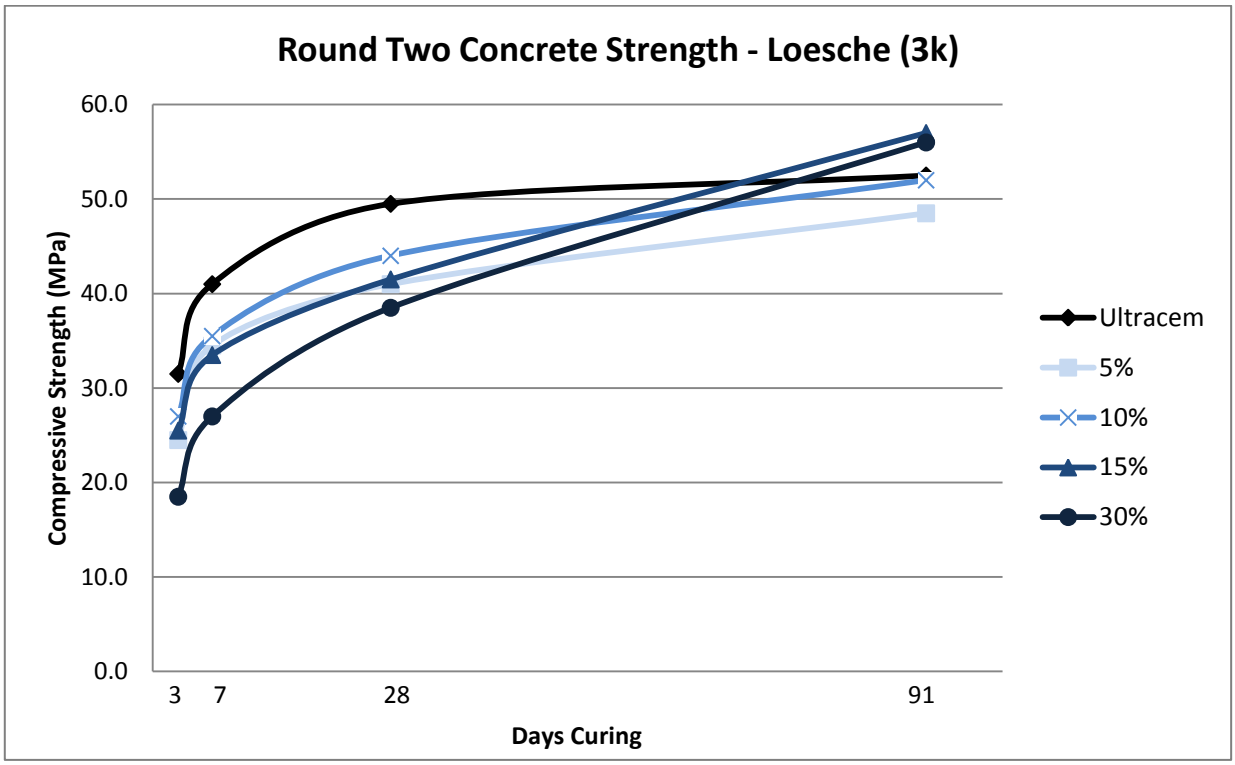

Figure 7.3: Round Two concrete strength – Loesche (3k)

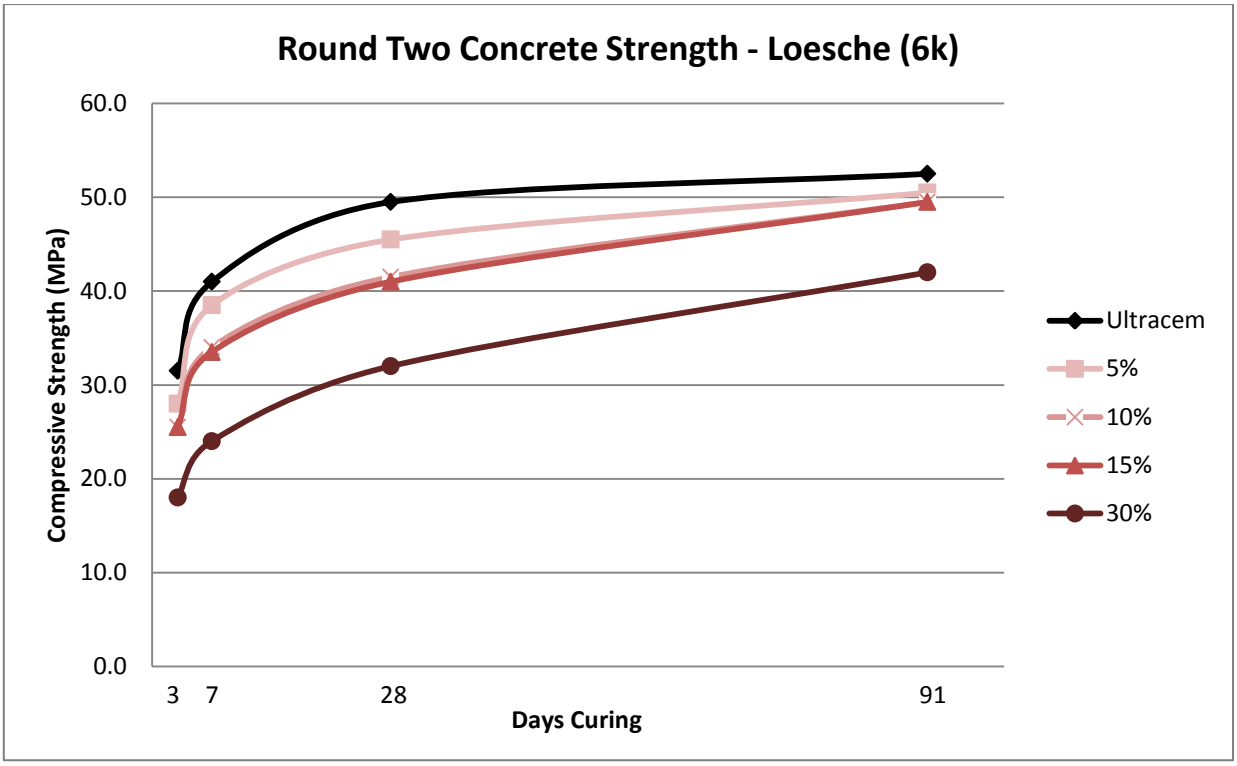

Figure 7.4: Round Two concrete strength – Loesche (6k)

7.1.1 Analysis of Pumice Replacement Rate

On examination of the 5% pumice replacement, Round One Loesche (3k) and Round Two Loesche (6k) are the best performing mixes at all ages (Figure 7.5). Relative to Ultracem, each returned 6% reductions in strength at 28 days. The former showed an increase at 91 days (+5%), the latter a small reduction (-4%). Round One Loesche (6k) returned relatively consistent reductions up to 28 days (-14-16%), with a small reduction at 91 days (-4%). Round Two Loesche (3k) was the worst performing mix at all ages, returning a 17% reduction at 28 days, still showing an 8% reduction at 91 days.

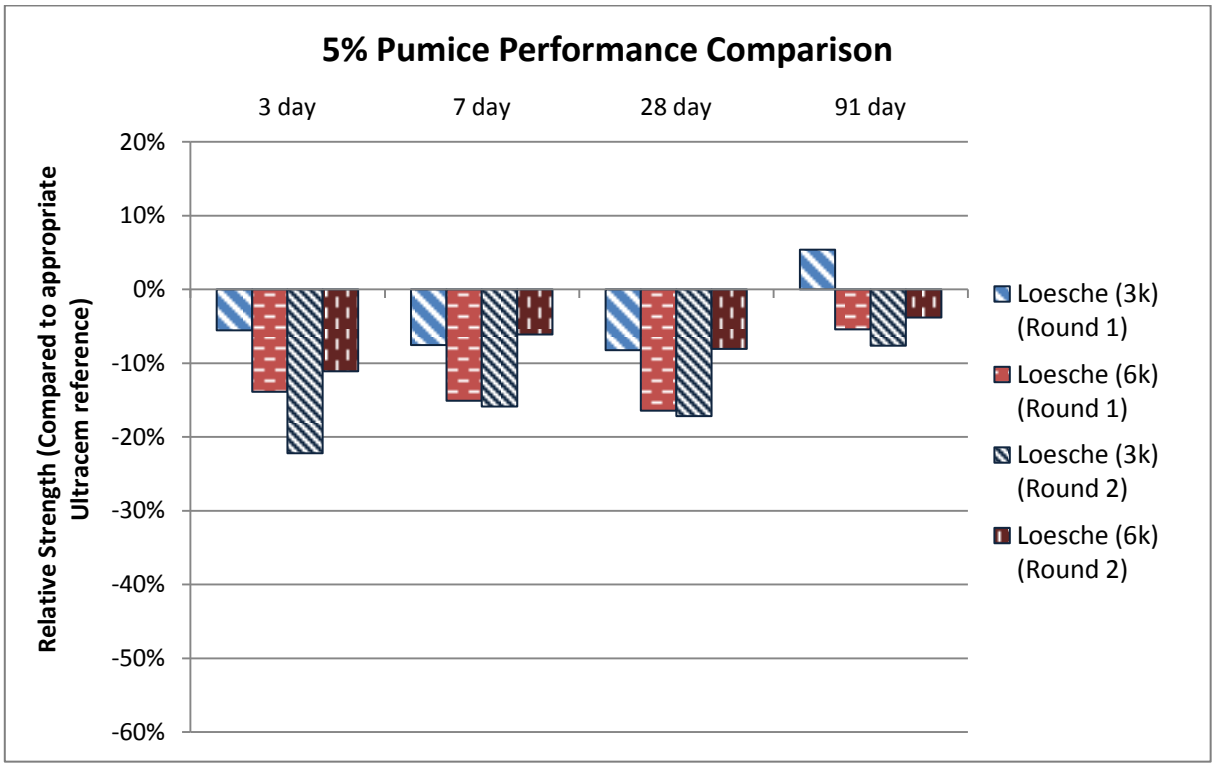

Figure 7.5: 5% pumice performance comparison

With 10% pumice, the Round One Loesche (3k) pumice sample was again the best performing mix at 3 and 7 days (Figure 7.6). Its relative performance worsened up to 28 days, where it returned a moderate reduction (-12%). By 91 days, this mix stands out with a significant improvement (+11%). Round Two Loesche (3k) returned a similar reduction at 28 days (-11%), and essentially achieved parity at 91 days (-1%). The remaining mixes (Rounds One and Two Loesche (6k)) both returned relatively poor 16% reductions at 28 days, then a 1% increase and 6% decrease at 91 days respectively.

These results can also be compared with preliminary trial mixes using 'Horotiu pumice'[1]. These returned very poor early strength results, with 26% and 19% reductions at 3 and 7 days respectively. Results did improve substantially by 28 days (-7%), surpassing all 'Rangiriri' (Loesche) pumice mixes in this selection. 91 day strengths were not tested in the preliminary trial.

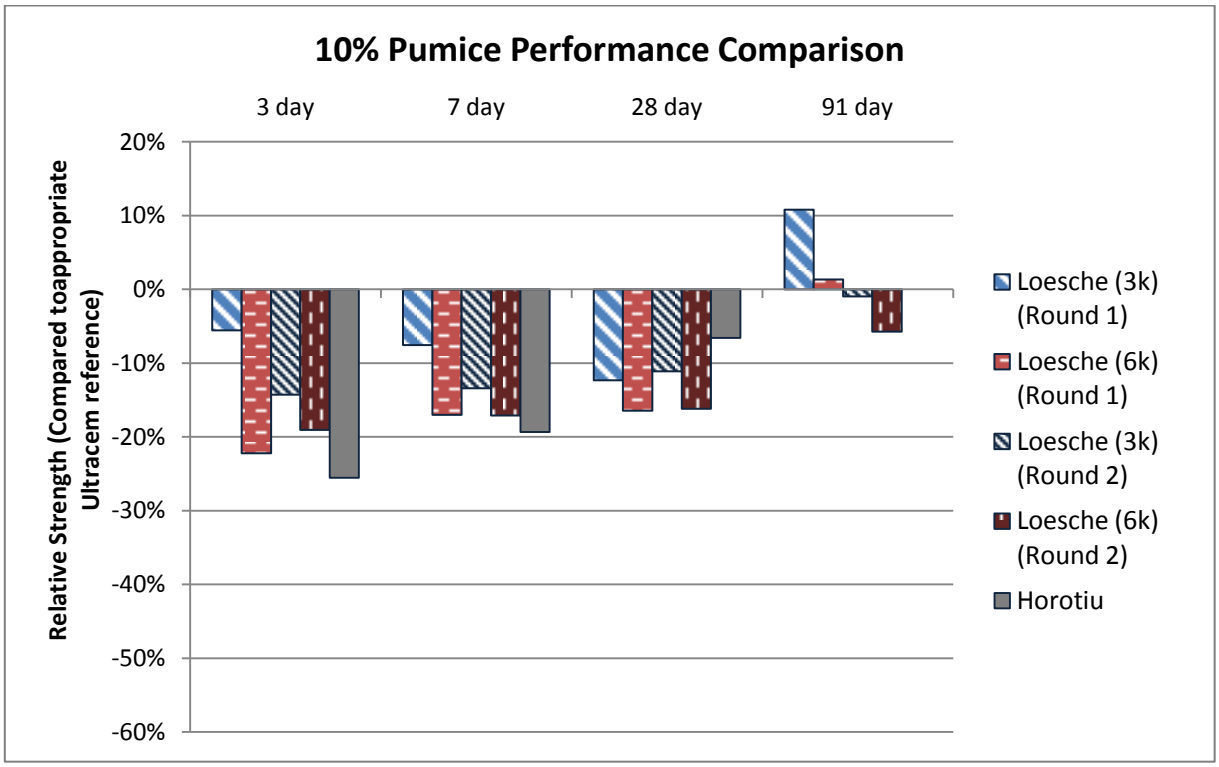

Figure 7.6: 10% pumice performance comparison

More significant strength reductions are recorded with the 15% pumice addition, and are relatively constant across all ages up to 28 days (Figure 7.7). At 3 and 7 days curing, reductions range between 18-25%. At 28 days, each mix returned a 16-17% reduction, with the exception of Round One Loesche (6k) (-23%). This mix was consistently the worst performing up to 28 days, with all strengths 23-25% below reference levels. All mixes showed substantial improvement at 91 days, with three of the four returning increases (1-9%) relative to their respective references. The remaining mix (Round Two Loesche (6k)) returned a 6% reduction.

[1] This was a preliminary trial conducted in January 2011, using 10% 'Horotiu pumice' and the Round One mix design.

Based on the general trend of decreasing performance with increasing pumice content, it was not surprising that the 30% pumice replacement performed extremely poorly up to 28 days (Figure 7.8). The best performing mix at 3 days was Round Two Loesche (3k) (-19%), vastly superior to the 43-53% reductions recorded in the remaining mixes. At seven days curing, the Round One Loesche (3k) mix returned the worst strength result across all Rounds of testing (-57%).

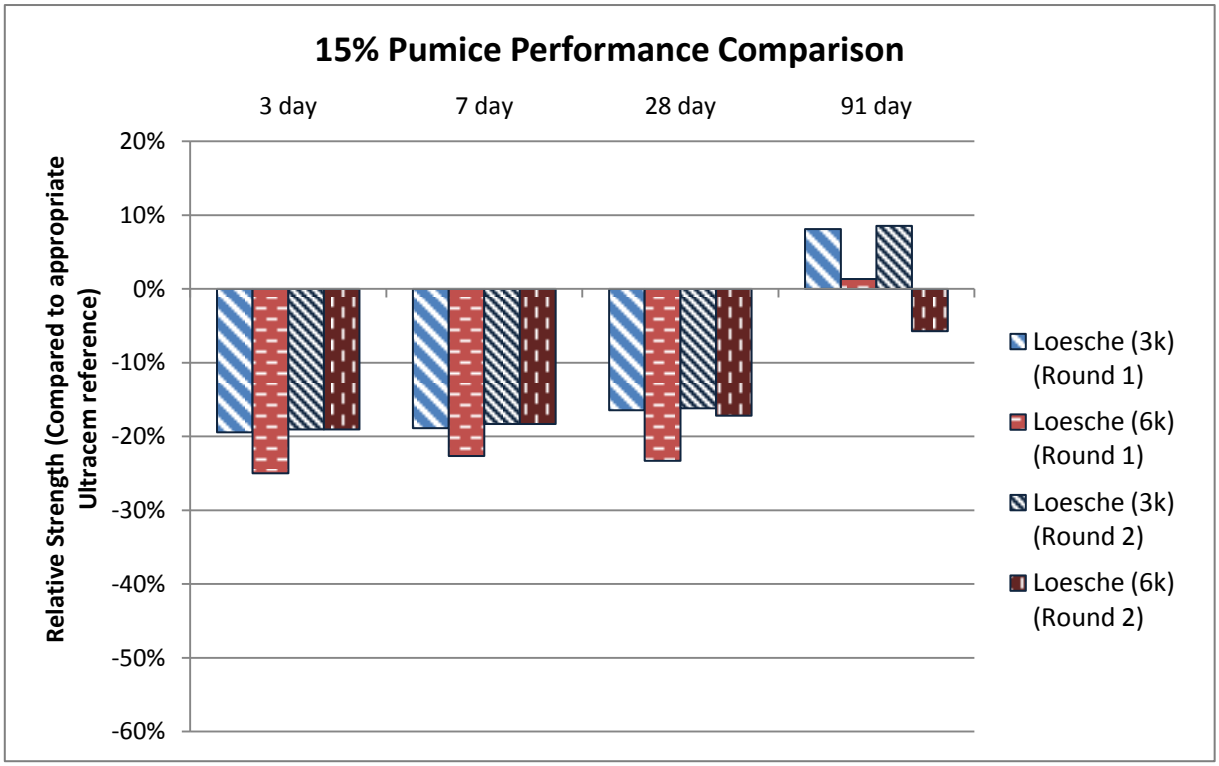

Figure 7.7: 15% pumice performance comparison

By 28 days, three of the four mixes returned >30% reductions in strength, the remaining mix (Round Two Loesche (3k)) returning a 16% reduction. This mix returned consistent 16-19% reductions at all ages up to 28 days. Results were variable at 91 days, with both Round One mixes returning 5% reductions, and Round Two mixes returning a 9% increase and 20% reduction respectively.

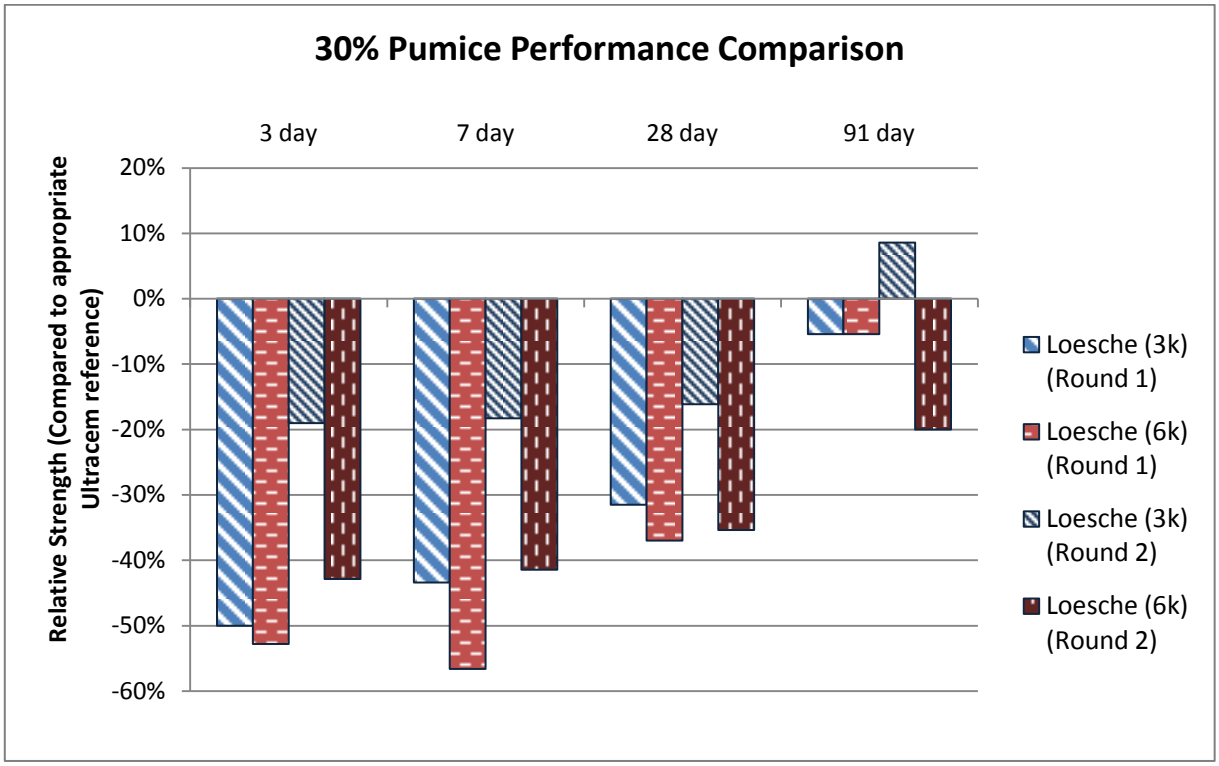

Figure 7.8: 30% pumice performance comparison

7.1.2 Optimisation of Pumice Replacement Rate

Pekmezci & Akyüz (2004) report that optimum pozzolan replacement rate can be measured using the ratio of pozzolan combined with cement. While substantial work has been undertaken in this field with the use of fly ash, and efficiency factors can be readily calculated, very little similar research has been done with natural pozzolans. Their study concludes that there is a maximum amount of pozzolan which can be used with optimum efficiency, maximising concrete strength.

Using their chosen pozzolan (a Turkish volcanic tuff), the optimal pozzolan/cement ratio was approximately 0.28. Pumice replacements from this thesis are presented with their corresponding pozzolan/cement ratio in Table 7.1, where it can be seen that this ratio would fall between 15 and 30% replacement. While this method holds true for the Turkish pozzolan, the ratio does not correlate well with milled Taupo pumice. In Rounds One and Two, Taupo pumice further degrades 28 day concrete strength with increasing replacement rate.

In Rounds One and Two, the reduction in strength observed between the 5% and 10% pumice addition is relatively minor, therefore the optimal rate may fall somewhere within

this range. South (2009) notes that in his study, the reduction in strength between 20% and 30% replacement is less than that between 10% and 20%. This was possibly due to more optimal packing density with higher pozzolan additions, acting as a fine aggregate.

Results gained in this thesis are reflected in a study by Targan et al., (2003), where blended mixes using another Turkish deposit were trialled at similar replacement rates[2]. Using this pozzolan, maximum 28 day concrete strength was achieved with 10% replacement, the only mix to surpass the reference, albeit marginally.

Commercially, an optimal replacement is likely to rely not only on concrete strength, but detailed cost analyses, and the marginal cost per unit strength. Additionally, while blended concrete strengths are below reference levels up to 28 days, several mixes have achieved strengths much closer to Ultracem at 91 days, which may further influence how the material may eventually be used. Improvements to the mix design, such as those of Rounds Three and Four, may again affect the optimal replacement.

Table 7.1: Pozzolan/Cement Ratio

Pumice Replacement	Pozzolan/Cement Ratio
5%	0.05
10%	0.11
15%	0.18
30%	0.43

7.2 Round Three Concrete Strength – Influence of High pH Water

Rounds Three and Four are discussed separately, with Round Three concrete strengths presented in

Figure 7.9. Again, strengths are below Ultracem up to 28 days, although parity has essentially been achieved at 56 days. Strength continues to trend upward at 91 days, again suggesting concrete strength will further develop with time. Concrete performance is discussed in detail in Section 7.5.2, and results are presented with respect to their curing time in Appendix 9.

[2] 5, 10, 15, 20, 25 and 30% replacement.

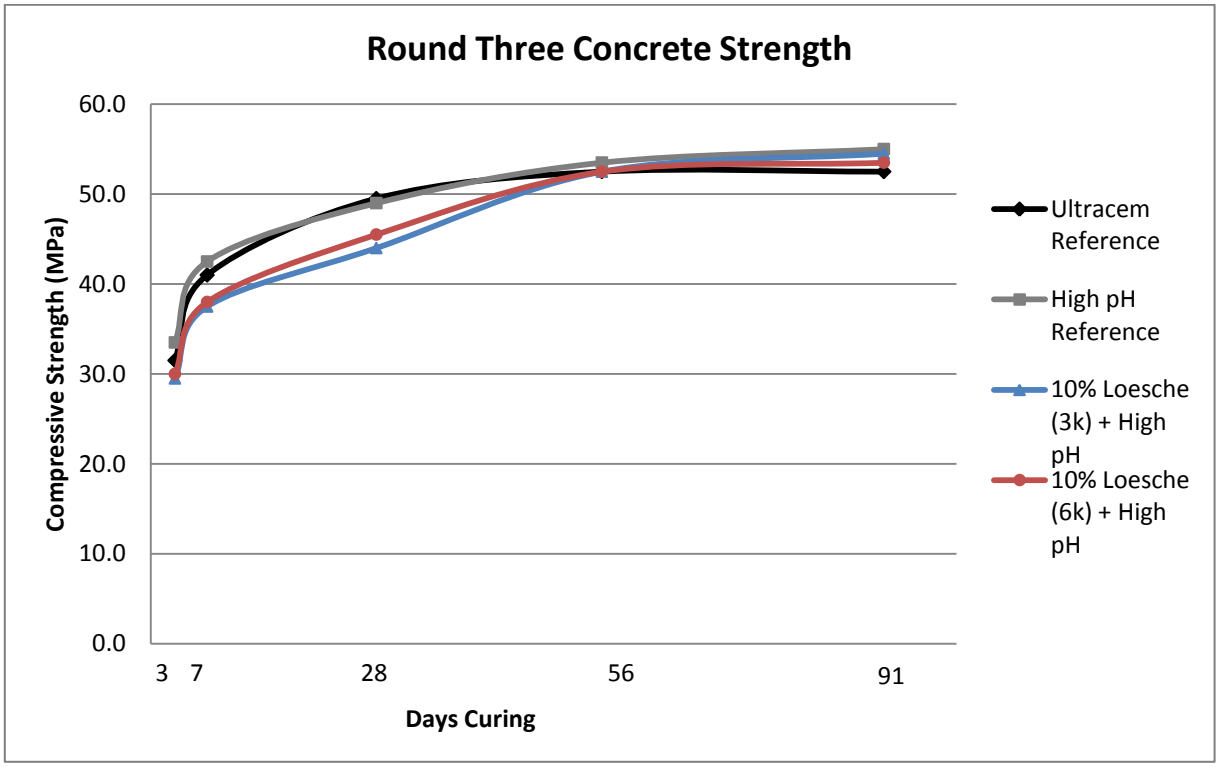

Figure 7.9: Round Three concrete strength

7.3 Round Four Concrete Strength – Influence of Superplasticiser

Round Four concrete strengths are presented in

Figure 7.10 and

Figure 7.11, and with respect to curing time in Appendix 10. As with all previous tests, blended concrete continues to develop strength at later ages, particularly the Loesche (3k) mixes. Again, all mixes are below Ultracem at 28 days, and performance comparisons are discussed in Section 7.5.3.

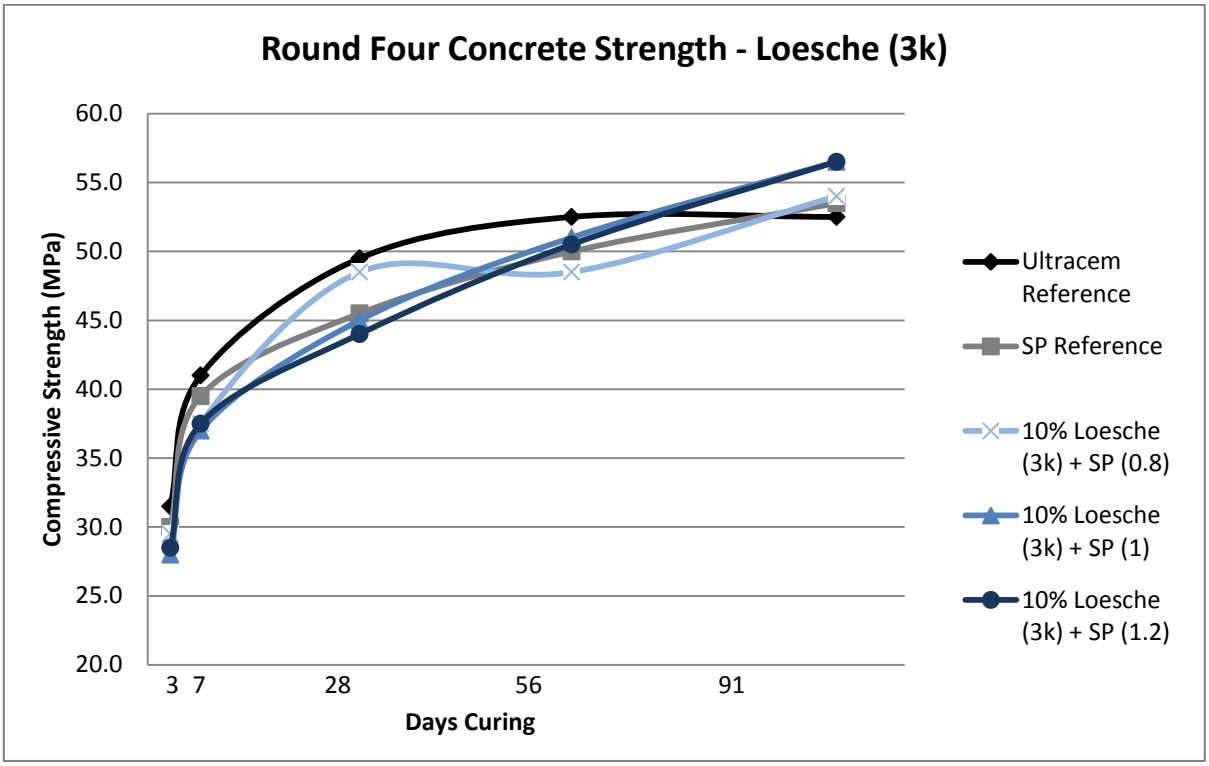

Figure 7.10: Round Four concrete strength – Loesche (3k)

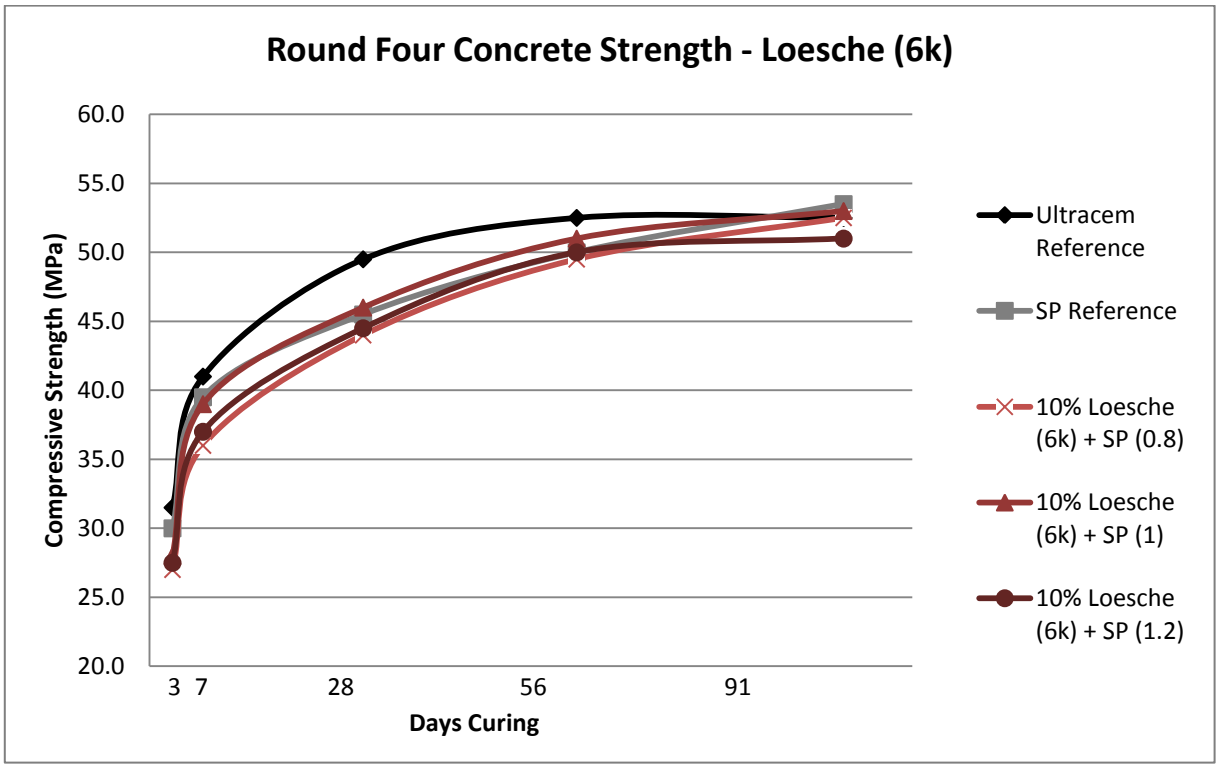

Figure 7.11: Round Four concrete strength – Loesche (6k)

7.4 Effects of Pumice Fineness

7.4.1 Round One and Two

In general, the finer Loesche (3k) pumice[3] performs better than Loesche (6k)[4]. Across Round One, Loesche (3k) strengths are 8-10% higher with 5% pumice replacement. This trend continues, with 10% replacement (+5-18%), 15% replacement (+5-8%) and 30% replacement (0-23%).

The general trend is similar in Round Two, with the exception of the 5% Loesche (6k) mix, which returned consistently higher strengths (4-13%) than its counterpart at all ages[5]. At 10% replacement, the reduction in Round Two w/b ratio has significantly reduced the difference in strength between pumice samples, where Loesche (3k) strengths are a much more consistent 4-6% higher.

At 15% replacement, this difference is virtually non-existent in Round Two samples up to 28 days, suggesting the reduction in w/b ratio has had no effect on relative concrete strength. By 91 days, more substantial variation can be seen between the pumice samples, where Loesche (3k) strengths were 15% higher.

At 30% replacement, the Loesche (3k) pumice performed substantially better in all Round Two mixes. This presents a particularly interesting situation, where at 91 days, it was 33% stronger than its counterpart. This is the largest variation recorded between the two pumice samples across all rounds of testing.

Shi & Day (2001) found that increasing pumice fineness did little to improve 28 day concrete strengths, as did South (2009). In this thesis, pumice fineness has only had a major influence on 30% replacement at w/b=0.5 (Round Two). No influence is recorded at w/b=0.6 (Round One), where 30% mixes are identical. This suggests that at lower w/b ratios, pumice fineness has a more significant effect on concrete strength.

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[3] SSA = 760 m^2/kg

[4] SSA = 492 m^2/kg

[5] Reasons for this performance reversal are inconclusive; however similar results are recorded in Round Three (see Section 7.5.2).

7.4.2 Round Three

Interestingly, with the use of high pH water, the coarser Loesche (6k) pumice performs slightly better than its finer counterpart up to 28 days curing. Although margins are slim, the consistent results across all three ages suggests high pH water may react with coarser pumice grains slightly quicker at early ages. By 56 days, no difference is recorded between the two pumice samples, and both have returned slightly lower (-2%) strengths than the high pH reference. By 91 days, the finer Loesche (3k) performs slightly better, and both returned slight reductions relative to the high pH reference. This suggests that by later ages, strength improvements shown in the coarser sample give way to the higher overall SSA of the finer pumice.

7.4.3 Round Four

While the SP dose rates were not able to be held constant across pumice samples (see Section 6.6), broad comparisons can still be made. At SP (0.8), the finer Loesche (3k) pumice performed consistently better at all ages except for a moderate reversal at 56 days. At SP (1), results are mixed, although the finer pumice appears to perform better overall, especially at 7 and 91 days. At SP (1.2), the finer pumice generally returns higher strengths, again with substantial differences at 91 days.

While the Loesche (3k) pumice generally performs better, clear trends attributable to pumice fineness are difficult to determine. The exception to this is at 91 days, where the addition of SP has had a positive influence on concrete strength with the finer Loesche (3k) pumice, regardless of SP dose rate.

7.5 Effects of Mix Variations

7.5.1 Round One and Two Performance Comparison

In Round Two, the w/b ratio was reduced from 0.6 to 0.5 (see Section 6.2). At 5% replacement, the coarser pumice mixes benefit from reduced w/b ratio, performing consistently better in Round Two (Figure 7.5). This was not observed in the Loesche (3k) mixes. At 10%, the same general trend exists (Figure 7.6), however the differences are far less profound. Loesche (3k) mixes performed relatively worse in Round Two, except at 28 days, where little difference is recorded. The Loesche (6k) mixes have recorded negligible variation between rounds.

At 15% replacement, virtually no change is recorded in relative strength between Rounds One and Two up to 28 days (Figure 7.7). The variation is however more marked at 30% replacement, where Round Two mixes generally return significantly higher strengths (Figure 7.8). This is particularly obvious in the Loesche (3k) mixes, especially up to 28 days curing (although little variation was recorded in the Loesche (6k) sample at 28 days). These results indicate that while absolute performance remains relatively poor, the reduced w/b ratio has substantially improved pumice reactivity at 30% replacement.

7.5.2 Round Three Performance Comparison

In order to properly compare the effects of high pH water and superplasticiser (SP), it is necessary to compare each round with its own respective high pH or SP reference mix, and then with Ultracem[1]. This allows the delineation of the effects of high pH water and SP on both Ultracem and pumice-cement blends.

When compared to the high pH reference, the relative performance of the 10% pumice concretes are poor (Figure 7.12). The Loesche (3k) mix returned strengths 12% below the high pH reference at 3 and 7 days, and 10% below at 28 days. The Loesche (6k) pumice returned 10% and 11% reductions at 3 and 7 days respectively, improving slightly to a 7% reduction at 28 days.

[1] Round Two reference (P11-027). See Section 1.1.1.

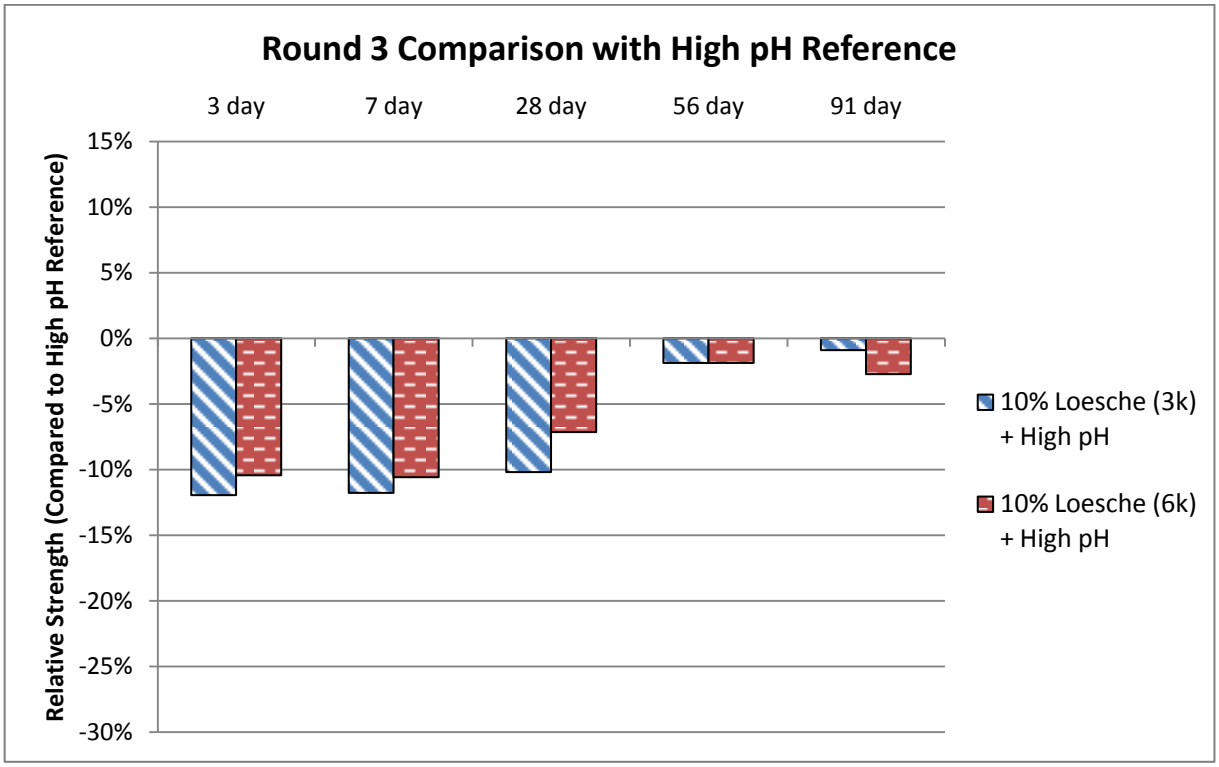

Figure 7.12: Round Three comparison with high pH reference
(N.B. 56 day strengths compared to 91 day Ultracem strength)

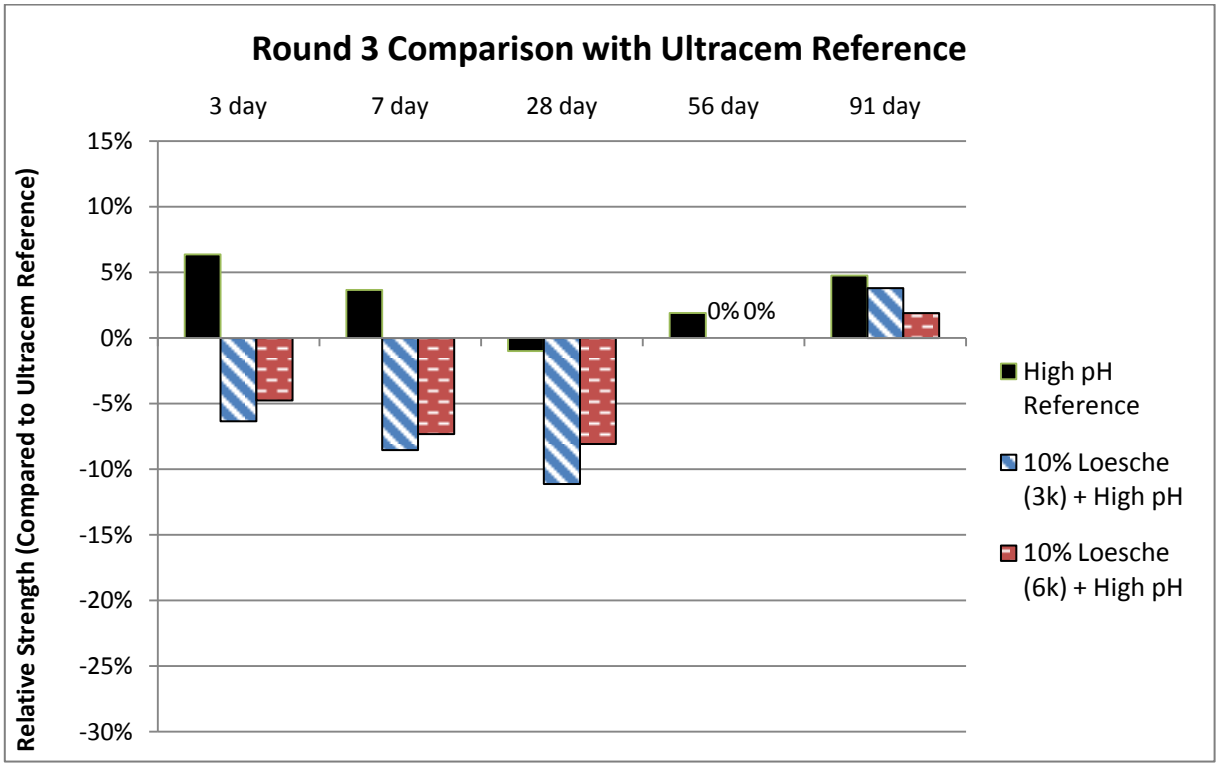

Figure 7.13: Round Three comparison with Ultracem reference
(N.B. 56 day strengths compared to 91 day Ultracem strength)

When compared to Ultracem, the high pH reference mix returned higher 3 and 7 day strengths, with 6% and 4% respective increases (Figure 7.13). This improvement was not observed at 28 days, although parity was essentially achieved (1% reduction). 56 day strength surpassed 91 day Ultracem[1], showing a 2% increase. By 91 days, the high pH reference showed a 5% improvement relative to Ultracem.

High pH concretes with 10% pumice returned 5-11% strength reductions up to 28 days (relative to Ultracem). By 56 days, both high pH blended concretes matched 91 day Ultracem strength, and showed 4% and 2% increases by 91 days. Ultimately, concrete made with high pH mix water appears to perform slightly better than Ultracem overall, but at the critical age of 28 days, no significant change is recorded. The addition of 10% pumice results in strength reductions relative to both the 28 day high pH and Ultracem references.

7.5.3 Round Four Performance Comparison

Comparing Round Four strength is slightly more complicated due to the varying superplasticiser (SP) dosage rates between pumice samples, where the Loesche (6k) pumice required substantially higher amounts of SP to achieve an acceptable consistency (see Section 6.6). Comparisons are made with this variation in mind.

When compared to the SP reference mix (SP = 144ml/100kg binder), 3 and 7 day strengths are generally 5-10% lower than the SP reference. Two mixes have essentially achieved parity at 28 days, with 2% and 1% respective reductions (Figure 7.14). Of these, the Loesche (3k) + (0.8) SP mix (SP = 115ml/100kg binder) continued to show substantial promise at 28 days, returning a 7% increase. A small 3% drop was observed at 56 days, and no appreciable change noted at 91 days. All other samples achieved strengths very close to the SP reference at 28 days, ranging from a 1% increase to a 3% reduction.

56 day strengths show a similar trend, ranging between +2% to -3%. 91 day results show clear variation between pumice samples, with each of the Loesche (3k) mixes returning 1-6% strength improvements, and each Loesche (6k) mix returning 1-5% reductions. Even so,

[1] 91 day Ultracem strength is used as an indicative reference as no 56 day strength is available.

these results suggest that the use of SP in conjunction with pumice reduces overall concrete strength losses at 28 days and beyond, in several cases facilitating gains.

Relative to Ultracem, the SP reference mix showed reductions in strength, most importantly at 28 days where an 8% reduction was recorded (Figure 7.15). Under these conditions, SP had a deleterious effect on relative concrete strength until 91 days, where a marginal 2% increase was recorded. This result is in agreement with the use of naphthalene type SP, which although of different composition, was found to interfere with the hydration of cement, causing retardation in both plain and natural pozzolan blended concretes (Çolak, 2003).

The addition of 10% pumice further reduces the performance of these mixes relative to Ultracem up to 56 days, resulting in 5-14% reductions in strength at 3-7 days across all mixes, and up to 11% at 28 days. More promising however is the aforementioned Loesche (3k) + (0.8) SP mix, which achieved a 28 day strength within 2% of Ultracem. Of all tests conducted, this is the most promising mix at this age. Interestingly, this mix performed relatively poorly at 56 days, returning an 8% reduction, in contrast with the 3-5% reductions of all other mixes. By 91 days, strengths range between 8% increases to an isolated 3% reduction, again with the finer Loesche (3k) pumice outperforming its counterpart.

SP addition appears to be correlated with concrete strength, and further understanding of its effects will be required to establish an optimal dosage rate. In the case of the Loesche (3k) pumice mixes; less SP, while delivering less workable concrete, appears to result in higher 28 day strengths, with improvements noted with decreasing doses. The highest 28 day strength was recorded with the addition of SP at 115ml/100kg binder. In the case of the Loesche (6k) mixes, of the three trial rates, the mid-range SP dose of 271ml/100kg binder returns the highest strength (Table 7.2).

Table 7.2: 28 day concrete strength and SP dosage

Mix Description	28 day strength (MPa)	SP (ml/100kg binder)
10% Loesche (3k) + SP (0.8)	48.5	115
10% Loesche (3k) + SP (1)	45.0	144
10% Loesche (3k) + SP (1.2)	44.0	173
10% Loesche (6k) + SP (0.8)	44.0	217
10% Loesche (6k) + SP (1)	46.0	271
10% Loesche (6k) + SP (1.2)	44.5	325

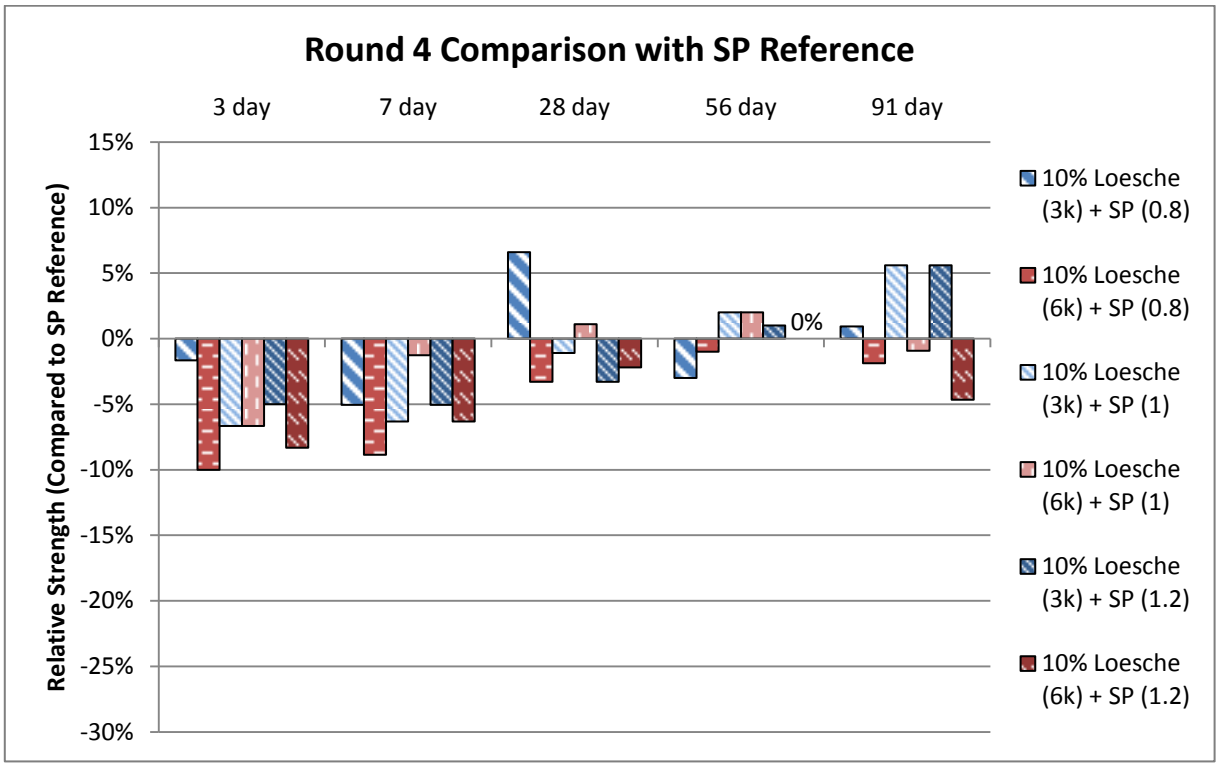

Figure 7.14: Round Four comparison with superplasticiser reference
(N.B. 56 day strengths compared to 91 day Ultracem strength)

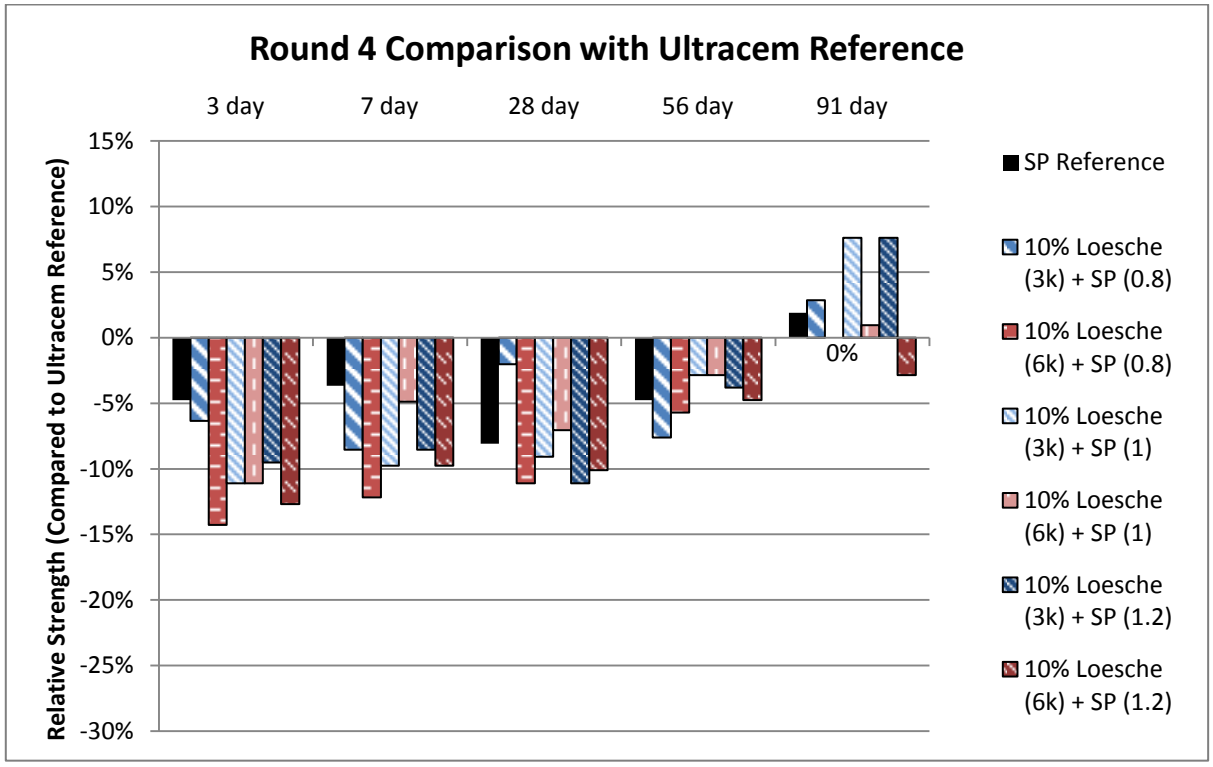

Figure 7.15: Round Four comparison with Ultracem reference
(N.B. 56 day strengths compared to 91 day Ultracem strength)

7.5.4 10% Pumice Inter-Round Performance Comparison

To further assess the strength performance of the various trial mix designs, 10% pumice concrete strengths are directly compared at 28 and 91 days (Figure 7.16). Here, strengths are reported as a mean of all tests in each round, giving a broad comparison.

Round One and Two concretes both returned 14% mean strength reductions at 28 days, where Rounds Three and Four returned 10% and 8% reductions respectively. All rounds showed moderate improvements at 91 days, except for Round Two (-4%). The highest mean 91 day strength increases (+6%) are recorded in Round One.

With the addition of 10% pumice, adjustments made to the Round Two mix design have had no effect on mean 28 day strength. The use of high pH mix water and SP have improved relative concrete performance, with results on average 10% and 8% below Ultracem respectively. Based on these results, the best 10% blended mix performance is with the addition of SP, and further dosage optimisation is likely to provide further strength improvements.

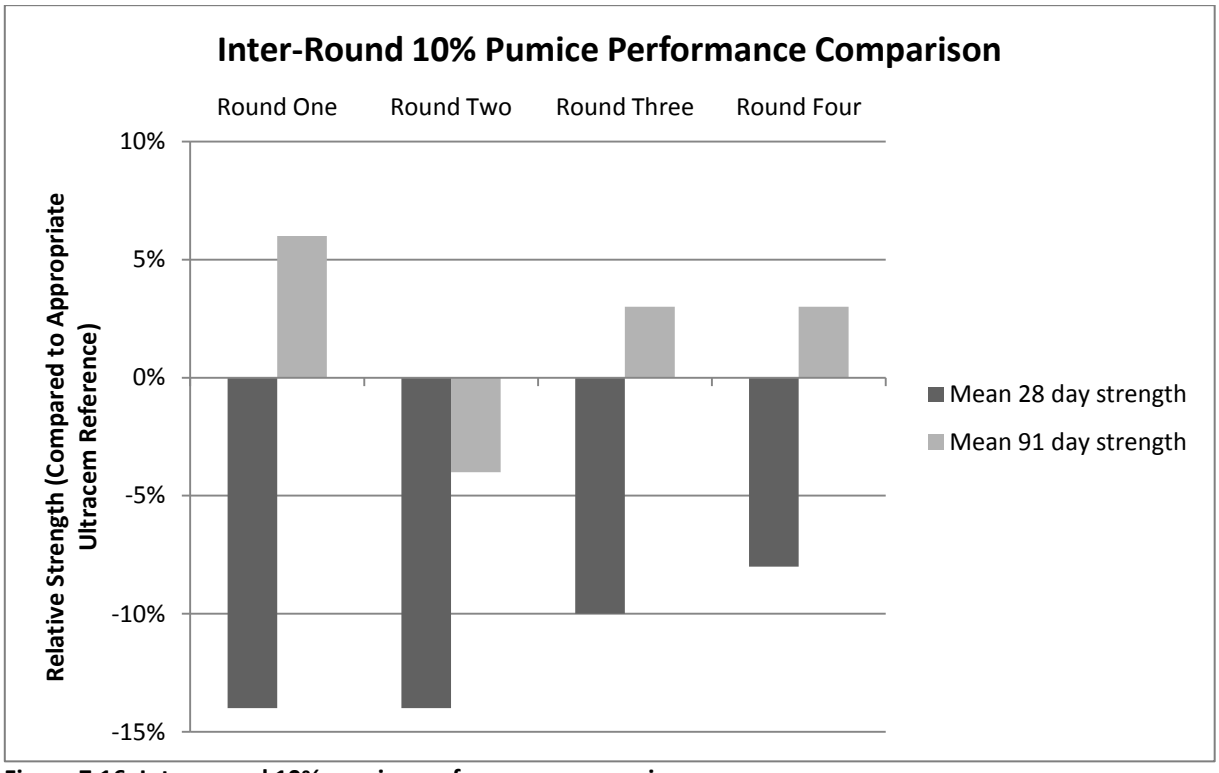

Figure 7.16: Inter-round 10% pumice performance comparison

7.6 Comparison with New Zealand Studies

Recent New Zealand trials have given mixed results. South (2009) trialled blended mixes with 10, 20 and 30% Rotoiti pumice, at 400, 500 and 700 m^2/kg. Early strengths were more significantly influenced by the addition of natural pozzolan (up to 30% replacement), and later age concretes were stronger than the reference. 28 day reference strengths were exceeded with the addition of 10% pozzolan, although the addition of 20 and 30% resulted in 6-9% reductions. When comparing pumice of different fineness, little variation was recorded in 28 day concrete strength. 90 day strength was however enhanced by increasing pumice SSA, which has generally been the case in this thesis.

Brown (1998) trialled 'Horotiu pumice', incorporating several mix variations. Several 30MPa mixes achieved strengths roughly equivalent to OPC at 28 days, again with reduced early strengths. In this study, while some mixes achieved or exceeded 28 days OPC strength, the best results were achieved by adding pumice not only as a cement replacement, but as a partial sand replacement (essentially reducing w/b ratio). Other mixes were trialled using oversubstitution and various superplasticisers, and returned lower 28 day strengths than those achieved in this thesis. It is also noted that some evidence suggests this pumice was contaminated with an unknown quantity of residual cement from the milling and packaging process (see Section 3.3), which may have resulted in slightly higher strengths.

7.7 Concrete Durability

Several aspects of concrete durability, including the influence of natural pozzolans, were assessed in Chapter 4. Concrete durability is an important aspect in determining the service life of concrete structures, and can be improved through the use of supplementary cementitious materials (SCM's) such as milled pumice.

Due to a testing problem, the 91 day 30% pumice bulk diffusion samples were excluded from these results. There was however an opportunity to assess chloride diffusion (and other durability properties) after prolonged curing, utilising remaining cylinders. These specimens were left to cure for as long as practically possible, and were assessed at 231 days (33

weeks). The following sections present the results of porosity, electrical resistivity and bulk diffusion testing carried out using blended cements.

7.7.1 Porosity

With 10% pumice, concrete porosity is not significantly affected at any age (Figure 7.17). The Loesche (3k) sample has a marginally lower porosity at 7 and 28 days than its counterpart, however both show equivalent porosities at 91 days (11.5%). Beyond this, the finer pumice is more slightly more porous at 231 days.

Both 30% pumice mixes are more porous than Ultracem at 7 days. Each show a rapid reduction in porosity at 28 days, followed by a period of very little change up to 91 days, where they are slightly more porous than Ultracem. At 231 days, the finer Loesche (3k) pumice has a porosity of 10.5%, slightly lower than its counterpart (11%).

The difference between all samples at 231 days is relatively small, with porosities ranging between 10.3-11%. It was anticipated that the increase in fine material would reduce overall concrete porosity, however Ultracem is still (marginally) the least porous at 231 days. As with other features of these blended concretes, porosity is still improving at 231 days, trending downwards and suggesting further improvements with age. Interestingly, this is also true of Ultracem, where other parameters (eg. strength, electrical resistivity and resistance to chloride) have not improved significantly (relative to blended mixes) beyond 28 days.

While the addition of 30% pumice has increased overall porosity, the effects are relatively small. Ultimately, the addition of this pumice has had little effect on concrete porosity, and the variance recorded here may be partially a result of slightly different compaction and workability.

Although the addition of pumice increases the total binder fine fraction, the fine pumice particles which replace cement are actually porous themselves. Pumice micro-porosity was explored in Section 6.4.3, and observed visually using SEM in Section 5.4. The reduction in

overall particle size may to an extent be countered by the increased porosity of the pumice itself, even when very finely milled.

One of the features which has not been investigated here is whether pumice pores retain their structure throughout the hydration process, and if so, for how long. Presumably, particles are either consumed during hydration, or partially or wholly replaced by C-S-H gel. Until this point, they may adversely affect concrete durability by increasing total porosity. Understanding this aspect will require further testing.

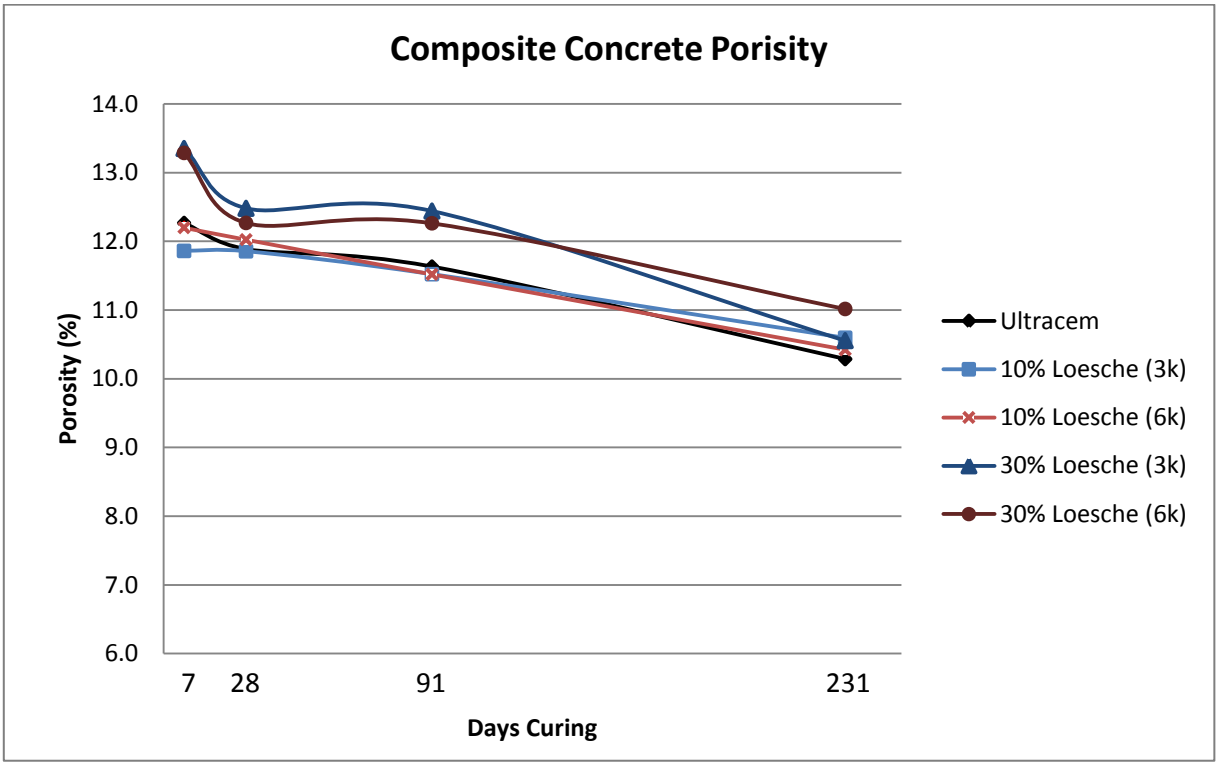

Figure 7.17: Concrete porosity

7.7.2 Electrical Resistivity

With the addition of 10% pumice, concrete resistivity was unaffected up to 91 days curing, however by 231 days, a significant increase was recorded (Figure 7.18). The addition of 30% pumice showed notable increases at 91 days, with massive increases at 231 days (Figure 7.19). At 91 days, 30% pumice concrete durability improved substantially compared with the relatively modest gains in concrete strength.

After 231 days curing with 10% pumice, the resistivity was 78% higher than Ultracem in the Loesche (3k) sample, and 71% higher in the Loesche (6k) (Figure 7.20). The addition of 30% pumice showed no significant variation at 7 or 28 days, however 81% and 42% improvements were recorded at 91 days. The most substantial improvement was seen at 231 days, where the respective electrical resistances are 359% and 244% higher than Ultracem (Figure 7.21)[2].

Very little variation was recorded between pumice samples at 10% addition, even at 231 days. With the addition of 30% pumice, the difference was significant, and the Loesche (3k) mix was notably more resistant at both 91 and 231 days. Both pumice samples continued to trend upwards at 231 days, where Ultracem reached a plateau. As with concrete strength, this suggests that further improvements in resistivity may be realised beyond 231 days. Increased resistivity may partially be explained by a reduction in pore solution pH in addition to the refinement of the microstructure of the paste.

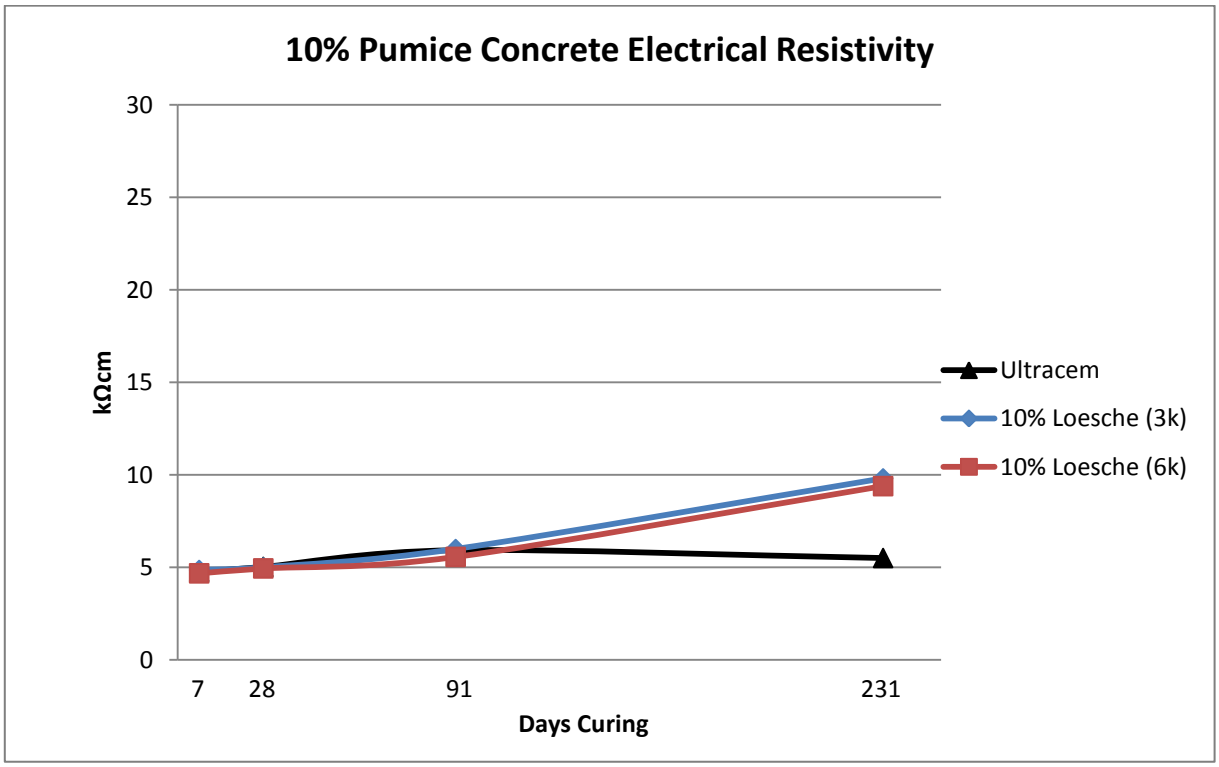

Figure 7.18: 10% pumice concrete electrical resistivity

[2] Note the difference in scale used in Figure 7.20 and Figure 7.21.

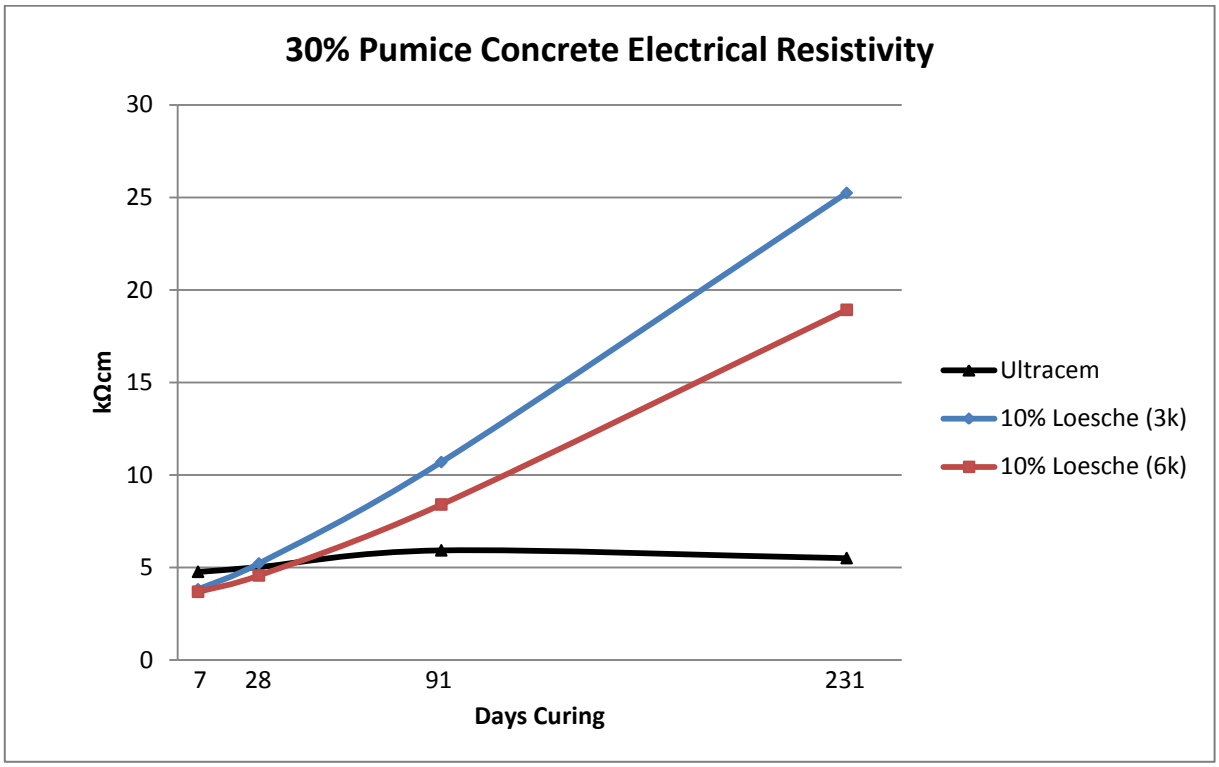

Figure 7.19: 30% pumice concrete electrical resistivity

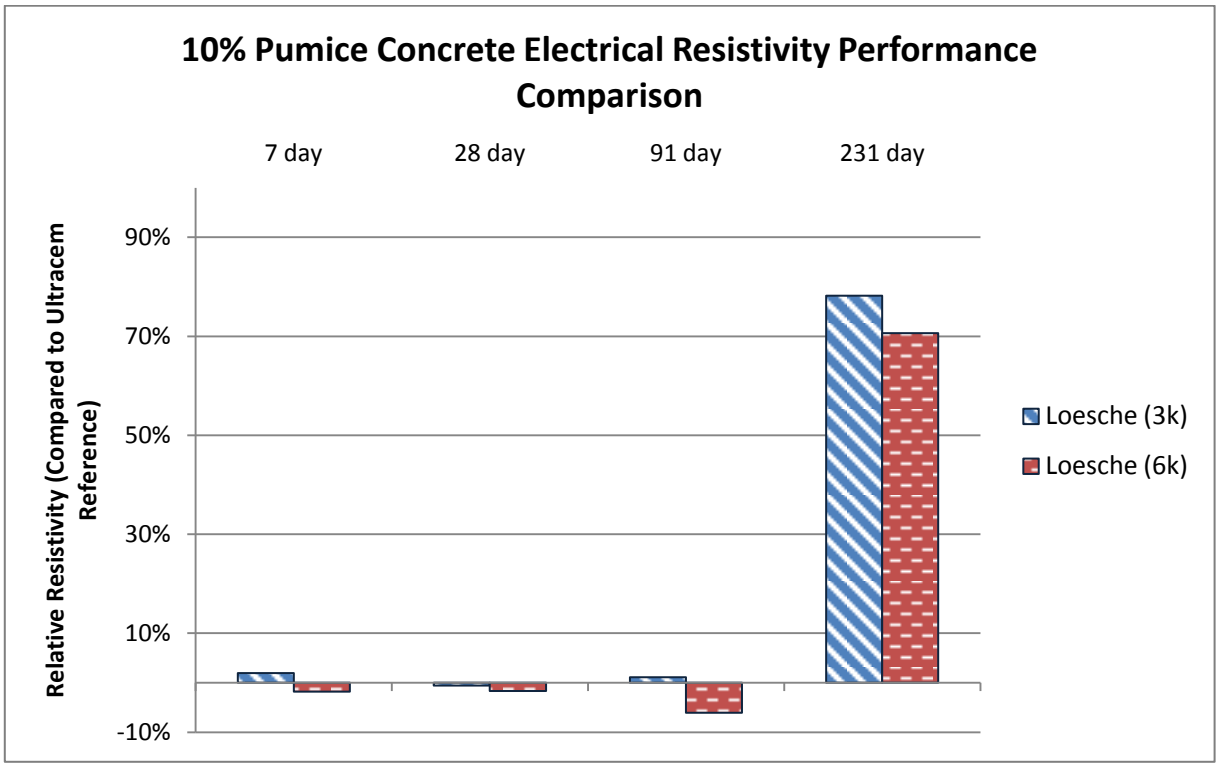

Figure 7.20: 10% pumice concrete resistivity performance comparison
(Note difference in scale)

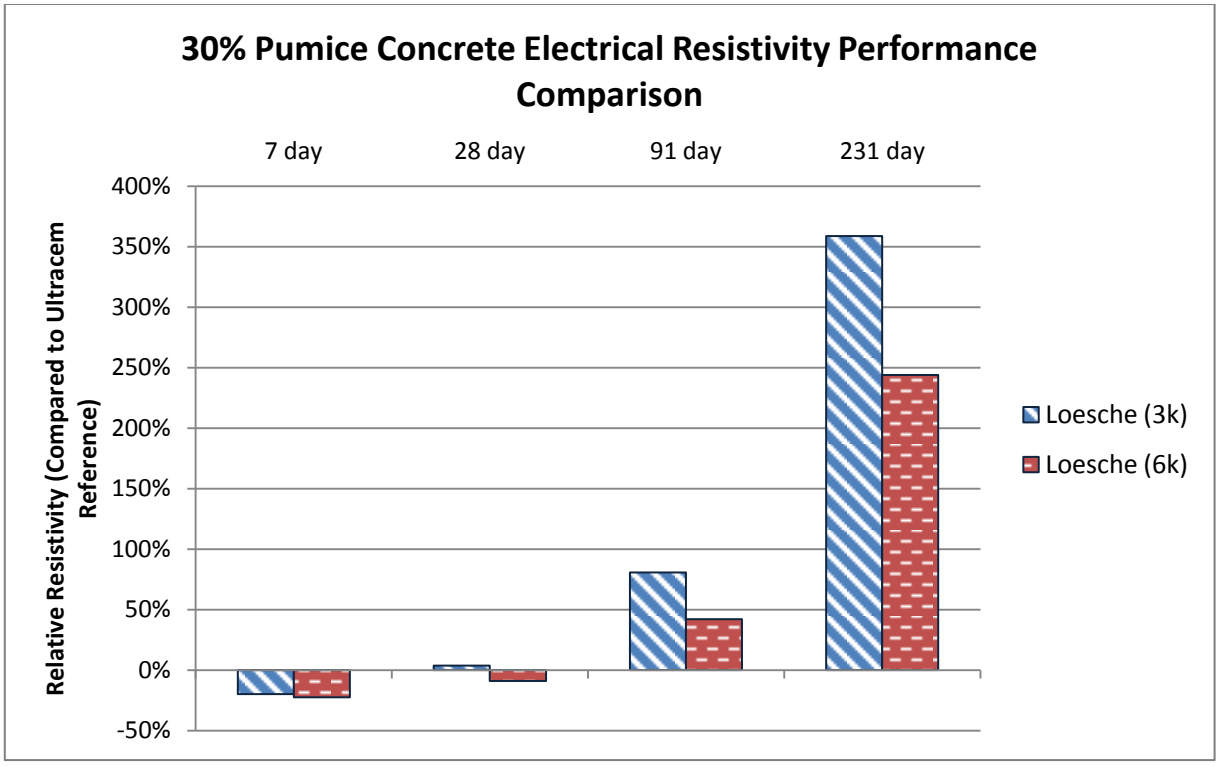

Figure 7.21: 30% pumice concrete resistivity performance comparison
(Note difference in scale)

7.7.3 Bulk Diffusion

At 28 days, Ultracem generally had lower chloride concentrations than all blended concretes, although the 10% Loesche (3k) sample returned similar results (Figure 7.22). This was the best performing of the blended mixes. The remaining mixes had higher diffusion coefficients, all above 2.20×10^{-11} m^2/s (Table 7.3).

At the deepest point measured (18-20mm), Ultracem returned the lowest overall chloride concentrations (0.02% mass of concrete). Blended mixes ranged between 0.04-0.09%, the highest concentrations recorded equally in the 10% and 30% Loesche (6k) samples.

Ultracem showed little change between 28 and 91 days (Figure 7.23), with only an 11% reduction in diffusion coefficient. Both 10% Loesche samples also showed modest improvements, with 26% and 22% reductions compared with their respective 28 day coefficients, essentially matching Ultracem. Ultracem again had the lowest concentration at 18-20mm depth (0.01%), compared with Loesche (3k) (0.03%) and Loesche (6k) (0.05%). The 91 day 30% pumice results were anomalous due to suspected contamination, and were excluded from this research. Results are presented in Appendix 11 for reference only.

At 231 days, Ultracem has shown very little improvement over its 28 or 91 day results, indicating little improvement in chloride resistance beyond 28 days (Figure 7.24). However, each blended concrete showed substantial improvements, especially those with 30% pumice. At the deepest point measured, no chloride was detected in either of the 30% pumice samples. Pumice fineness has also had a more substantial influence, where concrete containing the finer Loesche (3k) pumice showed improved resistance both at 10 and 30% addition when compared to Loesche (6k).

Compared with respective 28 day diffusion coefficients, the 10% Loesche mixes have shown moderate improvements at 231 days. The 10% Loesche (3k) coefficient is approximately 2.5x lower, and the 10% Loesche (6k) coefficient is ~1.75x lower. More substantial reductions are seen in the 231 day 30% Loesche (3k) coefficient, which is almost 4.7x lower, however by far

the most substantial improvement is seen in the 231 day 30% Loesche (6k) coefficient, which is almost 5.5x lower.

All 231 day diffusion coefficients are lower than that of Ultracem. The 10% Loesche (3k) and (6k) mixes returned diffusion coefficients approximately 2x and 1.5x lower than Ultracem respectively. More substantial difference was seen at 30% pumice replacement, where the Loesche (3k) coefficient was almost 5x lower than Ultracem, and the Loesche (6k) coefficient was almost 4x lower. These show significant reductions in chloride diffusion coefficient, and indicate real potential for use as a durable concrete.

Chloride concentrations from several field and laboratory studies have shown that quality concrete has a typical diffusion coefficient of about $2.0x10^{-12}$ m^2/s, but may be significantly lower in concretes containing SCM's (NIST, 1998). This corresponds well with diffusion coefficients using Taupo Pumice in this research. A review of chloride diffusion coefficients from other similar studies show lower coefficients than those achieved in this research, however several of these studies have focussed on significantly lower w/b ratios.

A Japanese study by Ampadu et al., (1999) tested various cement-fly ash blends, at several w/b ratios. Those most comparable with this research tested 40% fly ash at w/b ratios of 0.45 and 0.55. Diffusion coefficients were generally lower with reduced w/b ratio, and all were below those using Taupo pumice, ranging between $4.07x10^{-13}$ and $3.70x10^{-13}$ m^2/s (Ampadu, et al., 1999).

Tests by Li et al., (2011) using Chinese fly ash assessed chloride resistance at 28 days with w/b=0.35. Fly ash was added at rates between 10-40%, and all returned slightly lower diffusion coefficients than the cement reference. Diffusion coefficients ranged between $1.59x10^{-12}$ and $2.45x10^{-12}$ m^2/s. While these diffusion coefficients are very similar to those using Taupo pumice, they have been achieved with a much shorter curing period. This will be partially attributed to reduced w/b ratio.

A similar experiment by Leng et al., (2000) gave similar diffusion coefficients using another Chinese fly ash, and Chinese blast furnace slag. The w/b ratio (0.30) was again lower than

that used with Taupo pumice, and diffusion coefficients were again reduced. 28 day tests using 10% fly ash and slag returned diffusion coefficients of 3.84×10^{-13} and 4.16×10^{-13} m^2/s respectively, and 3.16×10^{-13} and 1.60×10^{-13} m^2/s at 40% replacement.

These comparative tests indicate that Taupo pumice performs well at similar w/b ratios, with similar levels of pozzolan replacement. Other tests using lower w/b ratio show significantly increased resistance to chloride, suggesting substantial durability improvements may be achieved using Taupo pumice at similarly low w/b ratios. Further testing of Taupo pumice will be required at a lower w/b ratio to determine the extent of the improvements in chloride resistance.

Table 7.3: Chloride diffusion coefficients

Chloride Diffusion Coefficients ($x10^{-11}$ m^2/s)			
Mix Description	**28 day**	**91 day**	**231 day**
Ultracem	1.92	1.71	1.84
10% Loesche (3k)	2.36	1.74	0.93
30% Loesche (3k)	1.75	n/a	0.38
10% Loesche (6k)	2.23	1.74	1.27
30% Loesche (6k)	2.68	n/a	0.49

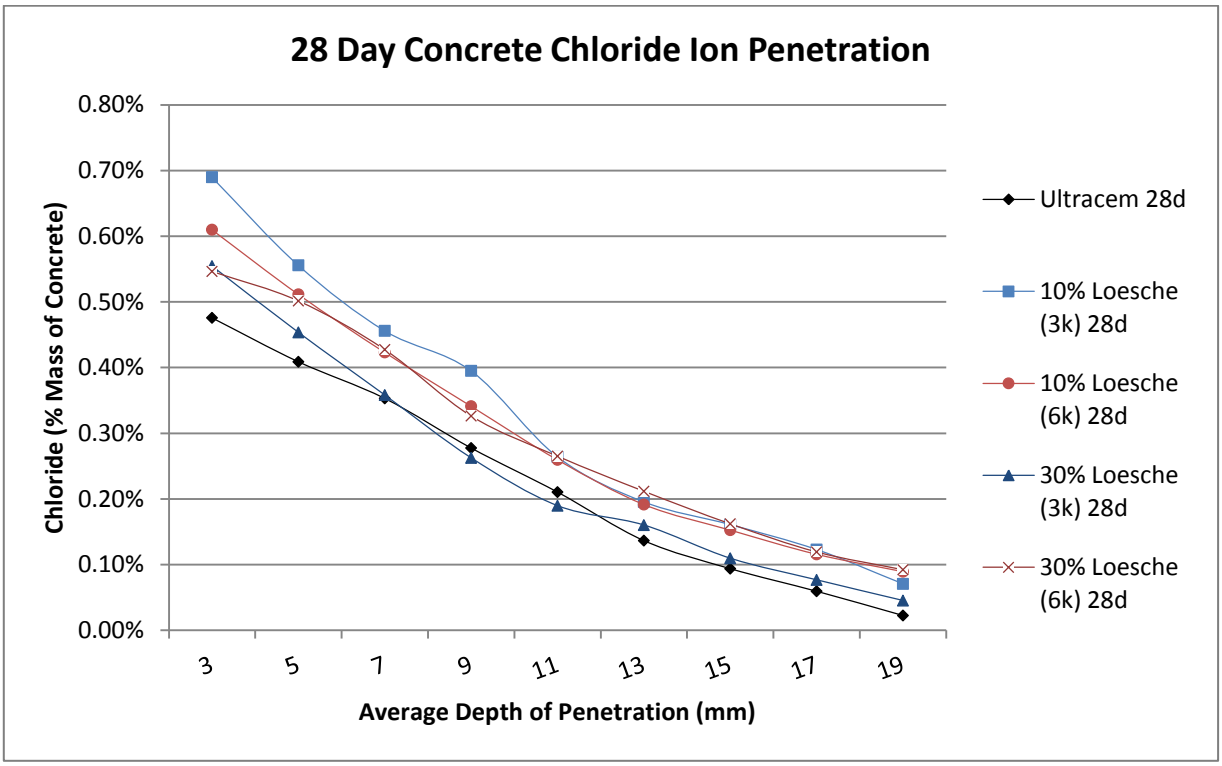

Figure 7.22: 28 day chloride ingress

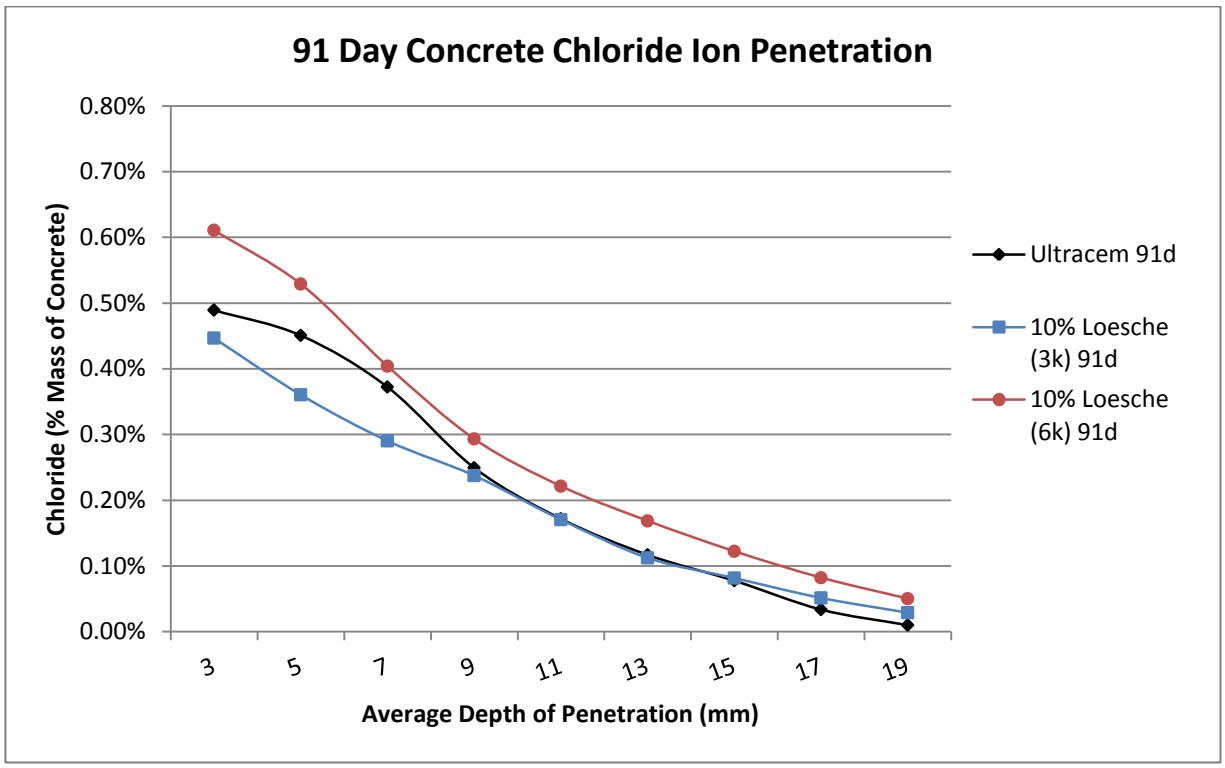

Figure 7.23: 91 day chloride ingress

(N.B. 30% pumice results are presented in Appendix 11 for reference only)

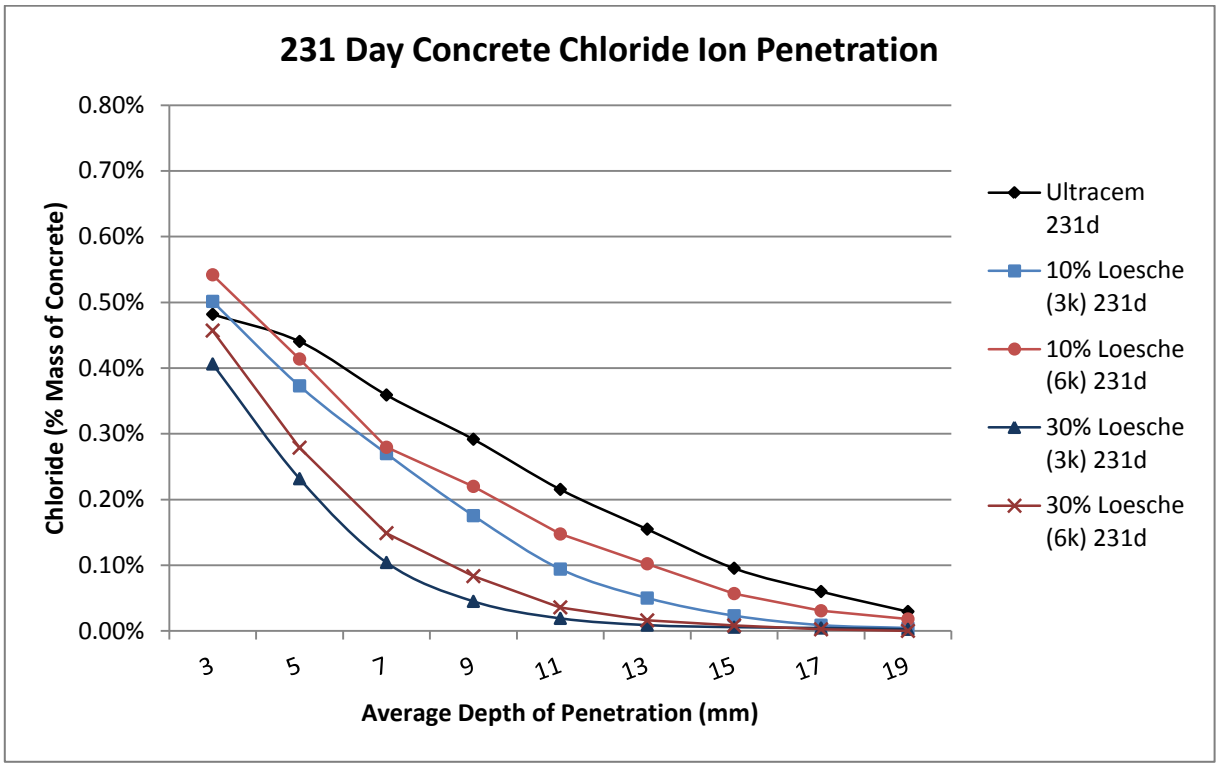

Figure 7.24: 231 day chloride ingress

7.7.4 Correlation of Durable Properties

To explore relationships between the investigated durable properties (ie. porosity, electrical resistance and bulk diffusion), pairs of results were plotted against each other, irrespective of curing time. Linear regression was then used to calculate the coefficient of determination (R^2).

Figure 7.25 shows the relationship between electrical resistivity and porosity. These two properties are not strongly correlated, with a relatively low coefficient of determination (R^2=0.37). The relationship between chloride diffusion coefficient and porosity is shown in Figure 7.26, which is slightly stronger (R^2=0.46). By far the strongest relationship is seen between electrical resistivity and chloride diffusion coefficient (R^2=0.93) (Figure 7.27). This shows that electrical resistivity is a good indicator of chloride diffusion coefficient, and is in accordance with other similar research (eg. Polder & Peelan (2002); Basheer, et al., (2002); Ampadu, et al., (1999)).

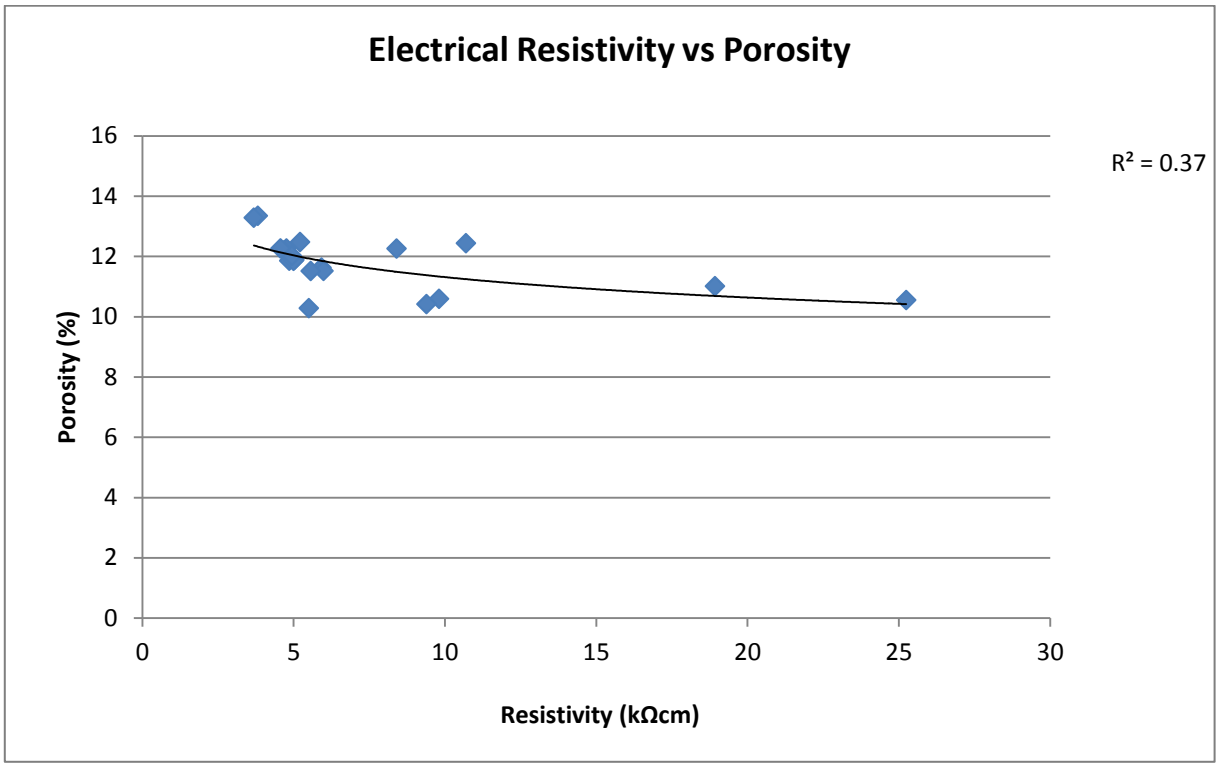

Figure 7.25: Electrical resistivity vs porosity

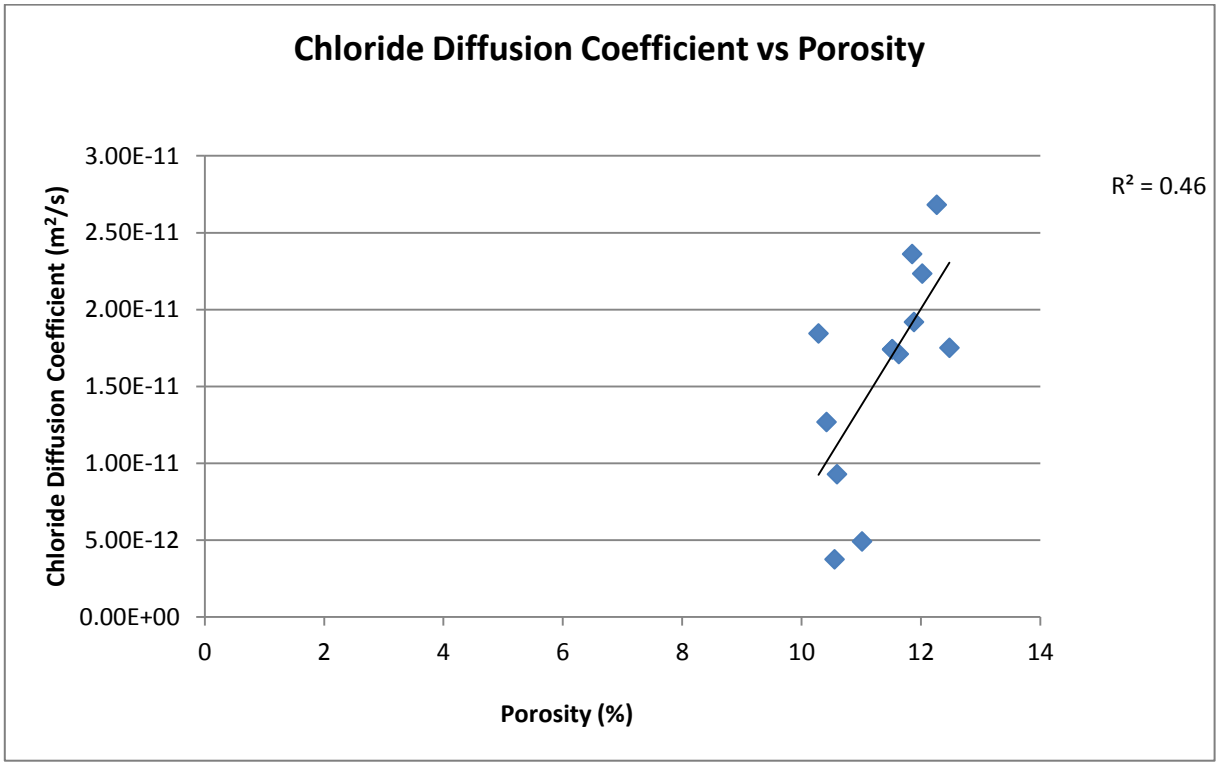

Figure 7.26: Chloride diffusion coefficient vs porosity

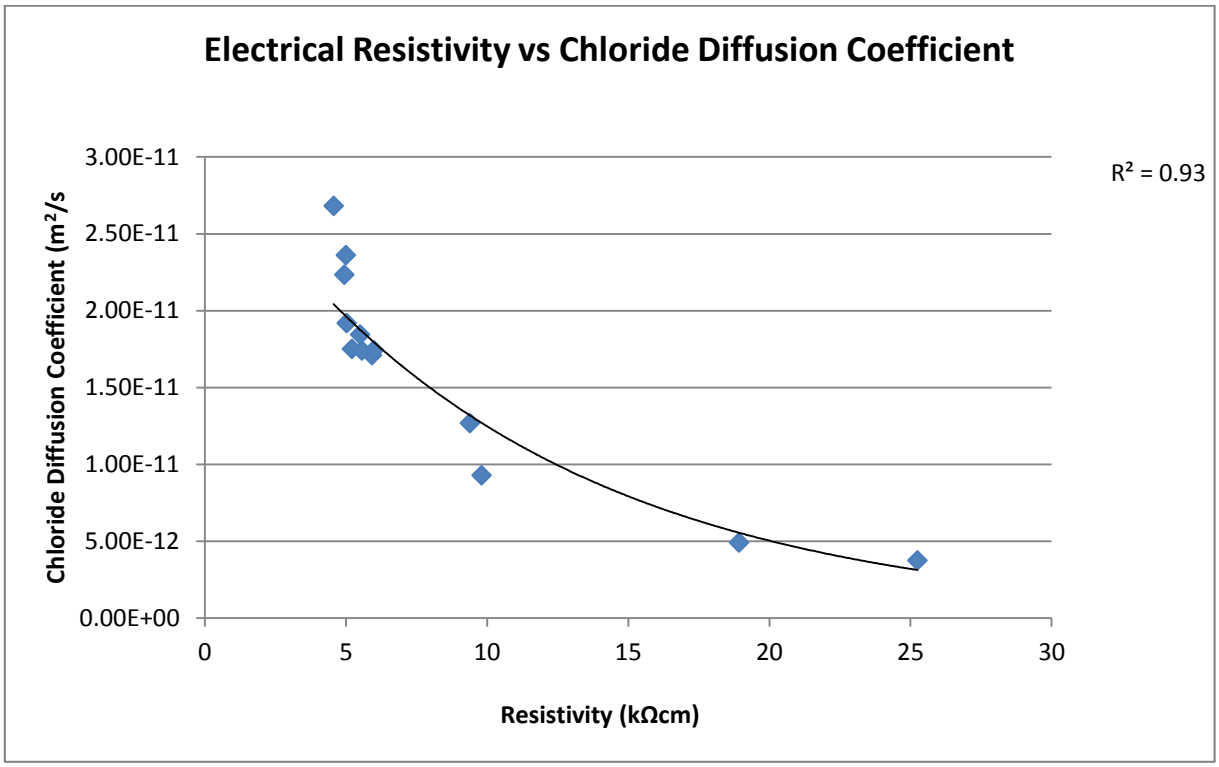

Figure 7.27: Electrical resistivity vs chloride diffusion coefficient

7.8 PozzoTech Analysis

7.8.1 Pumice Chemical and Mineralogical Properties

One of the principal components of PozzoTech analysis is the assessment of pumice mineralogy and geochemistry using XRF and XRD Rietveld analysis. These are presented in Table 7.4, with bulk chemistry of Rotoiti pumice (South, 2009), Horotiu pumice (Brown, 1998), typical fly ash and a Turkish volcanic deposit for comparison.

In the Taupo pumice, compounds considered beneficial to pozzolanic activity (SiO_2 + Al_2O_3 + Fe_2O_3) account for 86.89% of pumice mass (Table 7.4), well in excess of the minimum 70% specified by ASTM C 618[1]. Alkalis are present in crystalline and amorphous phases (4.04% Na_2O and 2.44% K_2O), where about half of the sodium is bound in plagioclase and therefore insoluble. Total organic carbon (TOC) is very low (0.16%), and is not likely to adversely affect concrete performance. Concentrations of Cl (0.11%) and SO_3 (<0.02%) are also very low. Of

[1] Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete

these compounds, only SO_3 has a specified maximum in ASTM C 618 (4%), this pumice being well below the limit.

Most of the pumice is amorphous glass (~70%), which has pozzolanic properties. The main crystalline phase is plagioclase feldspar (~25%), which is considered inert, and minor amounts of quartz and cristobalite were also detected (Holcim, 2011). Ultimately, from a chemical and mineralogical perspective, the composition of this pumice is well suited for use as a natural pozzolan.

Composition compares well with the Rotoiti pumice breccia tested by South (2009), and the fluvial 'Horotiu pumice' tested by Brown (1998). The primary pozzolanic compounds (SiO_2 + Al_2O_3 + Fe_2O_3) of the Rotoiti pumice totalled 84.69%, with traces of alkalis and calcium. The major compounds are present in very similar quantities to the pumice used in this thesis. Further analysis of a single Rotoiti pumice clast returned a lower silica content, and an increase in calcium. This was explained by differential magma cooling rates, where the larger clast underwent the formation of a more ordered crystal structure, reducing the glass content and allowing the formation of Ca_2SiO_4 (South, 2009).

Primary pozzolanic compounds of the 'Horotiu pumice' total 82.79%, and overall composition is very similar to the sample taken from Rangiriri. CaO levels are shown to be higher in the 'Horotiu' sample, which again indicates possible contamination during the processing of the material (see Section 3.3).

Compared with typical fly ash composition, Taupo pumice has a notably higher SiO_2 content, where fly ash contains more Al_2O_3 and Fe_2O_3. The Turkish pozzolan composition is comparable with fly ash. Pozzolanic compounds totalled 77.00% in the fly ash, and 78.77% in the volcanic deposit.

Table 7.4: Pozzolan chemical and mineralogical properties

	Taupo Pumice (Rangiriri)	**Taupo Pumice (Horotiu)**	**Rotoiti Pumice** (South, 2009)	**Typical Fly Ash** [1]	**Turkish Pozzolan** (Targan, et al., 2003)
Bulk chemistry by XRF (%)					
SiO_2	69.66	66.99	65.00	43.9	50.79
Al_2O_3	14.65	13.42	15.73	24.3	20.53
Fe_2O_3	2.58	2.38	3.96	8.8	7.45
CaO	2.20	5.70	5.66	7.0	6.56
MgO	0.48	0.79	0.93	1.9	3.74
SO_3	<0.02	-	-	1.7	0.08
K_2O	2.44	2.41	1.83	2.1	2.74
Na_2O	4.04	3.88	-	0.7	-
TiO_2	0.33	0.30	-	1.0	-
Mn_2O_3	0.08	0.11	-	0.07	-
P_2O_5	0.03	0.05	-	0.5	-
Cl	0.11	-	-	-	-
SrO	0.02	0.02	-	-	-
BaO	0.05	-	-	-	-
ZrO_2	0.03	0.02	-	-	-
LOI	3.31	3.95	2.91	5.4	10.17
Total	100.01	99.98	99.90	97.37	102.06
Mineral phases by XRD (%)					
Amorphous glass	~70				
Plagioclase feldspar	~25				
Quartz	<5				
Cristobalite	<5				
Other					
TOC (%)	0.16				
Methylene Blue Test (g/100g)	0.4				

7.8.2 Pozzolanic Reactivity Index

The pozzolanic reactivity index is a 28 day mortar compressive strength used to compare pozzolan quality across the Holcim Group according to the PozzoTech method. Results based on a 30% blend, and are expressed as a percentage of equivalent OPC mortar strength. The index shows favourable performance when compared with five other pozzolans used in the Holcim Group, achieving 82% of OPC mortar compressive strength at 28 days. Using this method, this pumice is deemed 'Sufficient' (Figure 7.28).

[1] Mean percentages of 41 fly ashes (Vassilev & Vassileva, 2007) .

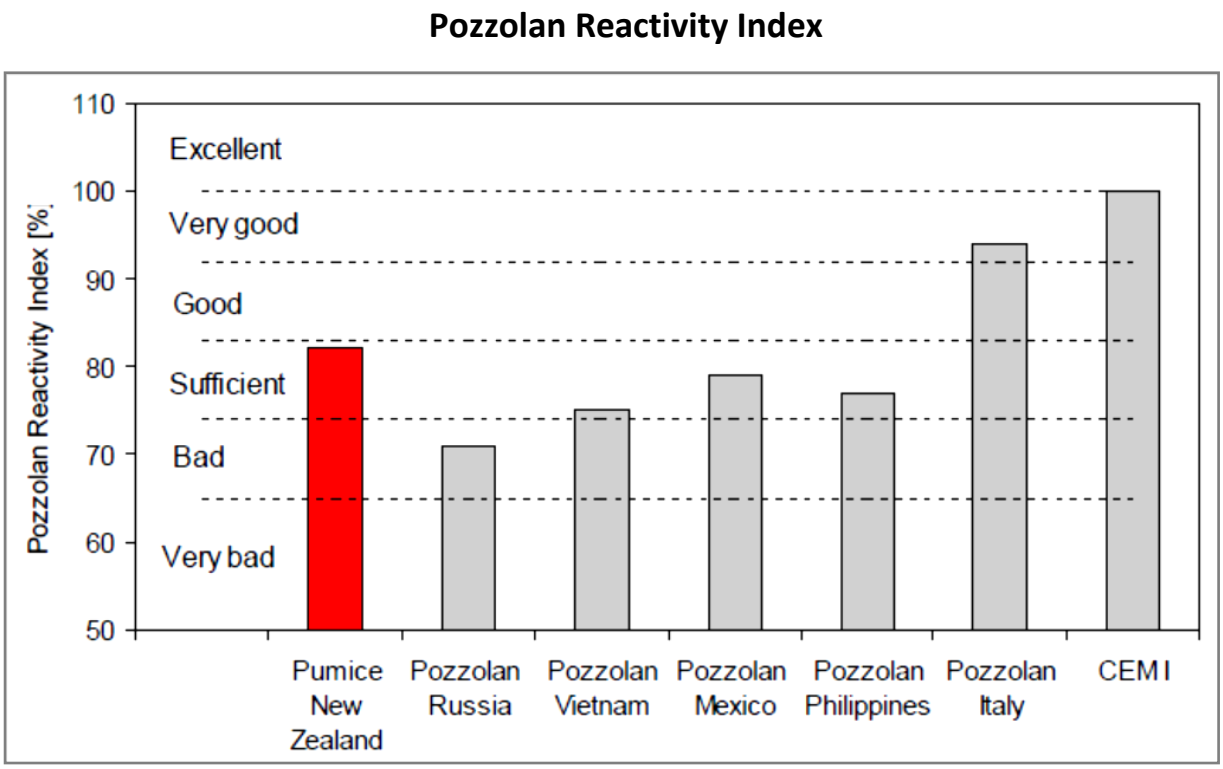

Figure 7.28: PozzoTech pozzolan reactivity index

7.8.3 Pumice Grindability

Pumice was ground to a target 45µm residue of 6-8%, recording the specific energy requirement. The actual 45µm residue was 3.8%, therefore the sample was over-ground. Taupo pumice performs favourably when compared with a selection of natural pozzolans, requiring 34.5kWh/t to exceed target fineness[2] (Figure 7.29) (Holcim, 2011). Achieving increased fineness consumes substantially higher amounts of energy, as was explored in Section 5.1, where the increase in pumice SSA (492 to 760m^2/kg) required almost three times the energy.

[2] These results refer only to the laboratory scale ball mill, and are not intended to fully represent an industrial milling system.

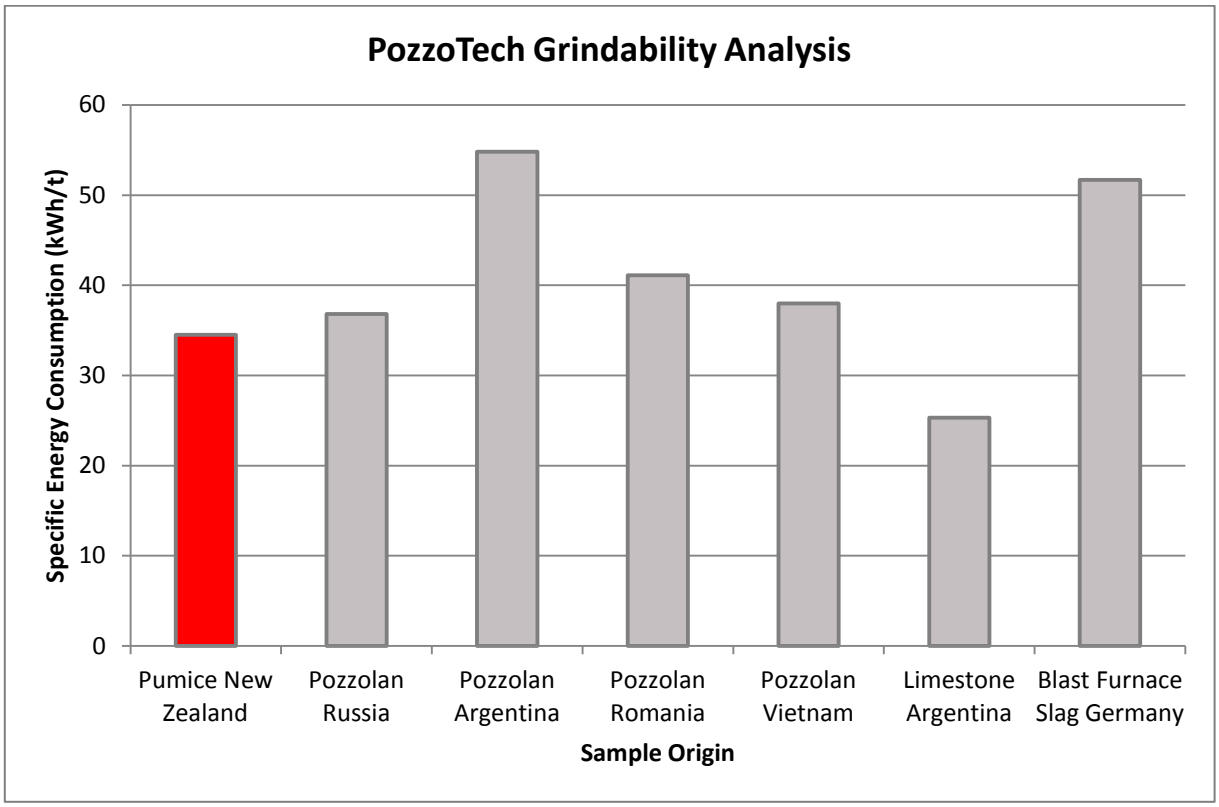

Figure 7.29: PozzoTech grindability analysis

7.9 Long Term Strength Development

Reduced early strength development is a well known problem associated with concretes containing natural pozzolans (eg. Shi & Day, 2001; Targan, et al., 2003; Bondar, et al., 2011), however significant improvements are often recorded after longer periods. Of the 28 trial mixes produced in this research, 14 returned 91 day strengths equal to or greater than their respective Ultracem references. Parity was not achieved in any trial concrete at 28 days. This shows that at some point between 28 and 91 days curing, the rate of pozzolanic reaction increases relative to Ultracem, contributing proportionally more to concrete strength at later stages.

The most significant improvement in concrete strength was recorded in the Round One 10% Loesche (3k) mix, where the 91 day strength was 11% higher than its Ultracem reference. It is of both academic and commercial interest to establish reasons for this, and if later stage strength improvements can be achieved earlier. For this reason, 56 day concrete strengths were tested in Rounds Three and Four to further refine time series strength development.

This essentially provided insight into the rate of reaction occurring between 28-56 days, and 56-91 days curing.

Figure 7.30 shows Round Three and Four cumulative concrete strength at 3, 7, 28 and 56 days as a percentage of 91 day strength. 91 day strength is considered here as an indicative 'final' strength, however as discussed throughout this chapter, trends in blended concrete strength indicate further potential improvements.

Cumulative strengths show a relatively wide spread at 28 days, where 78-90% of 91 day strength was achieved. Beyond this, the reaction slows, and by 56 days, 89-98% of 91 day strength had been attained. On average, concrete gained 11% strength between 28-56 days, but only 6% between 56-91 days. Therefore, beyond 28 days, most concrete strength development occurred in the 28-56 day period, slowing substantially beyond this. Figure 7.31 and Figure 7.32 show the actual strength development between the respective ages. Strength development between 28-56 days was relatively consistent across all Round Three and Four mixes, with seven out of eight showing increases of 10-16%.

The remaining mix (Loesche (3k) + SP (0.8)) mix fell outside this range, showing no strength development between 28 and 56 days. Further analysis of this mix shows a 21% increase between 3 and 7 days, within the range of other mixes, but then a 23% increase between 7 and 28 days, well above all others. This mix has undergone a rapid phase of strength development between 7 and 28 days, followed by a dormant period. 91 day strengths were within the range of other mixes. This may indicate a more optimal SP dose, and should be the target of future investigation.

Strength development between 56-91 days again presents interesting results, where each of the Loesche (3k) mixes with SP showed 10-11% gains, as opposed to the 2-6% gains recorded in all other mixes. This suggests that the finer pumice continues to gain relatively significant strength between 56-91 days with the use of SP, regardless of the SP dose rates trialled.

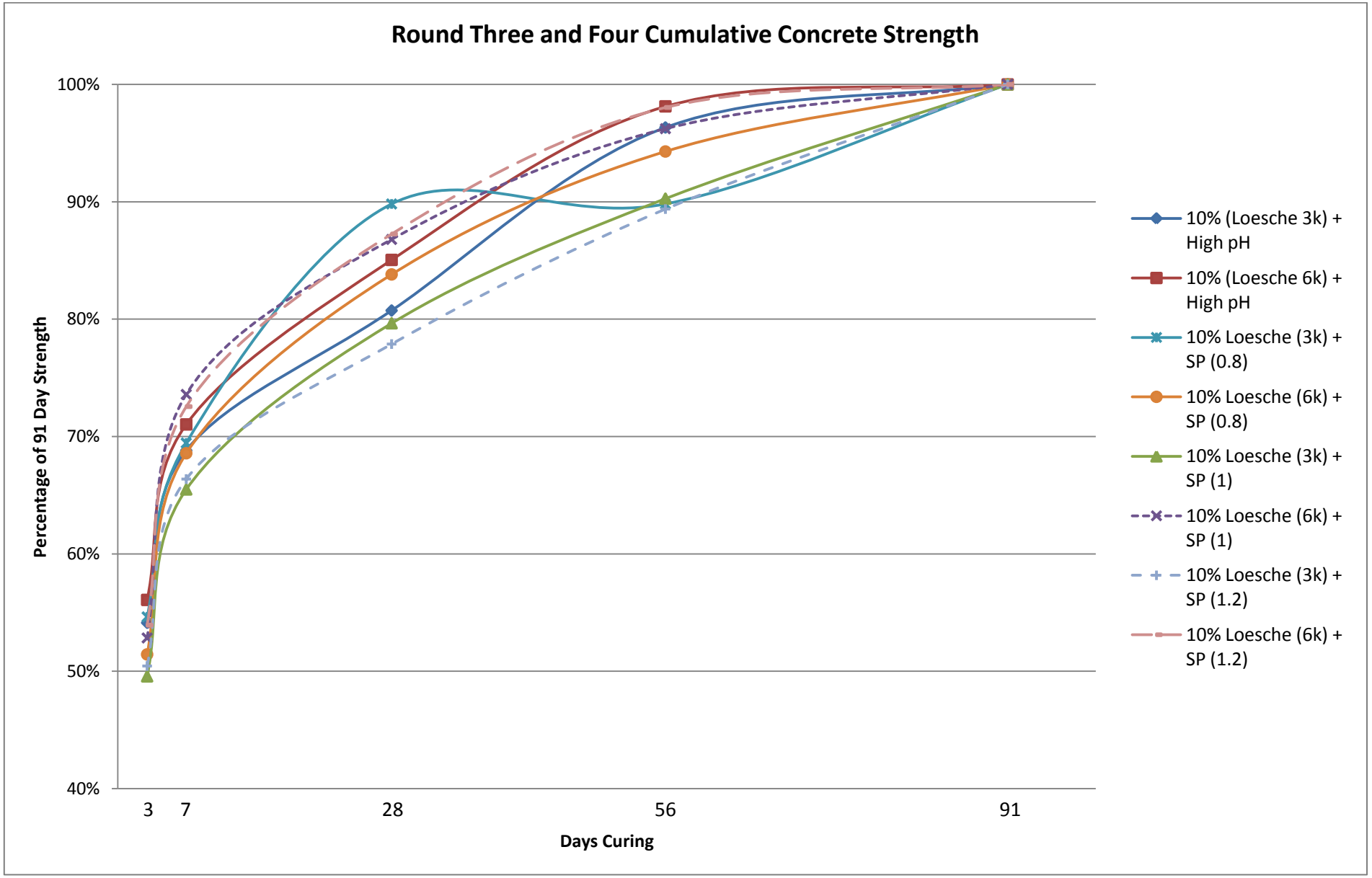

Figure 7.30: Round Three and Four cumulative concrete strength

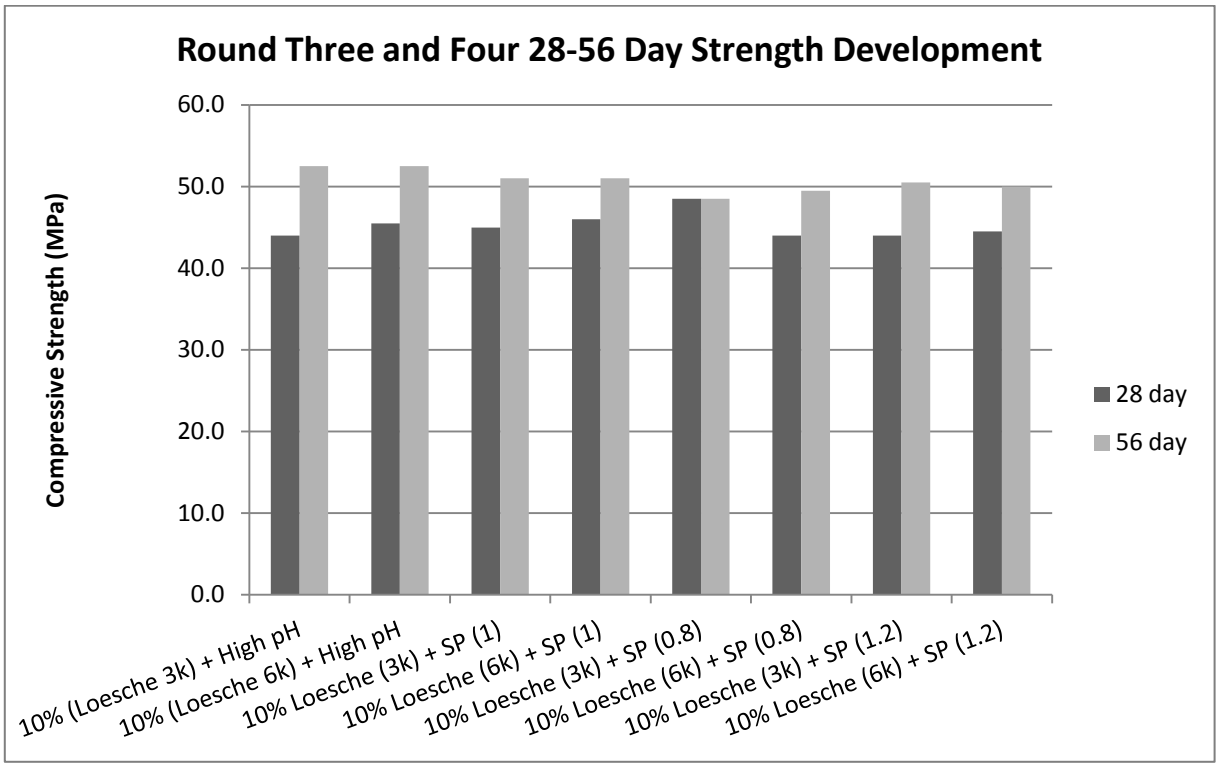

Figure 7.31: Round Three and Four 28-56 day concrete strength development

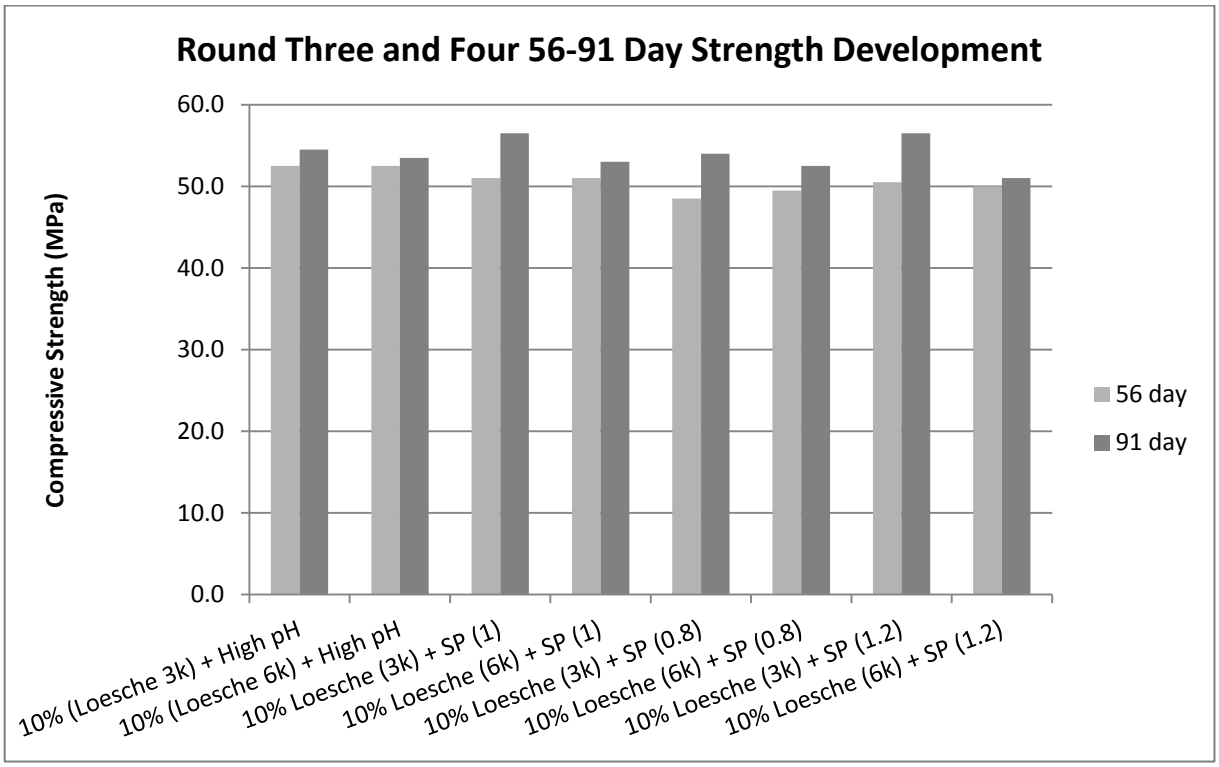

Figure 7.32: Round Three and Four 56-91 day concrete strength development

7.10 ζ-Potential

Given the variation in concrete strength recorded with varying SP dosages, the effects of SP and particle dispersion must be given further consideration. SP is a deflocculant, therefore establishing and quantifying the mechanisms by which it acts may provide insight into the optimisation of SP dosage and concrete strength. Consideration of ζ-potential gives the opportunity for such an insight.

When a solid surface comes into contact with an aqueous solution, an electric double layer develops at the interface. This consists of an immobile layer of ions charged oppositely to the surface, and a diffuse layer of hydrated ions. A shear plane is located near the boundary between these layers. ζ-potential is the potential at this plane (Elakneswaran, et al., 2009).

If all particles in suspension have a large positive or negative ζ-potential, they tend to repel each other rather than flocculate. Conversely, if particles have low ζ-potential, there is insufficient force to prevent particles flocculating (Malvern Instruments Ltd., 2004). Without SP, C_3S and C_2S have negative ζ-potential, whereas C_3A and C_4AF have positive ζ-potential. Each of these components show negative ζ-potential when dispersed with SP, therefore improving fluidity (Yoshioka, et al., 2002).

Understanding the magnitude and variability of milled pumice ζ-potential, and the influence of various SP types and dose rates will contribute to the overall understanding of particle interactions and material behaviour. Cement minerals do not adsorb SP uniformly, with C_3A and C_4AF adsorbing larger amounts of SP than C_3S and C_2S – regardless of the type of SP used (Yoshioka, et al., 2002). Additional components such as milled pumice and mineral limestone may further influence the interaction. For example, ground granulated blast furnace slag (GGBS) has a more significant effect on ζ-potential than Ordinary Portland Cement (OPC). GGBS, like milled pumice, has higher silica content than OPC. It produces a large amount of dissociated silanol[1], resulting in a more negative ζ-potential (Elakneswaran, et al., 2009). The effects of pumice on mix ζ-potential should be further investigated to allow optimisation of SP type and dosage, and ultimately, improved concrete strength.

[1]Weakly acidic, non-polar alcohols containing one or more SiOH groups (Sharma, 2012; Baxter, et al., 1997).

7.11 Workability

Concrete workability is a difficult parameter to define, and depends on a range of factors. The American Concrete Institute (ACI) defines workability as *"that property of freshly mixed concrete which determines the ease and homogeneity with which it can be mixed, placed, consolidated, and finished"*. Workability can be further explained as a property *"partially determined in the eyes of the beholder, who is influenced by the space to be filled with the concrete and the equipment required to assist in the placement and finishing process"* (Lamond & Pielert, 2006).

Concrete slump has traditionally been used to measure concrete rheology (flow properties), however the test does not encompass a full range of workability properties. Slump is a good indicator of one property of concrete workability (namely yield stress), however plastic viscosity (another important measurement) is not tested. Like concrete durability, no single test has been developed to adequately measure all properties relating to workability (Wong, 2001).

Achieving the workability and consistency required for industrial application of this product was beyond the scope of this research. From a material testing perspective, the only requirement here was that concrete cylinders could be adequately formed. Regardless, general inferences regarding concrete workability can be made using slump results, and observations from actually handling the material.

Ultracem reference mixes were based on target slump mix designs, which aimed to achieve a slump of 100mm ± 20mm. Most test mix slumps were within this range; however these did not necessarily exhibit the same finishing characteristics as Ultracem of equivalent slump. For example, blended mixes could return slumps of 100mm and be quite difficult to work, or return 70mm slumps and remain quite workable. Throughout all testing, it became evident that while increased pumice addition generally reduced concrete slump, the actual influence on workability was not as simple as might have been assumed.

Workability was not significantly affected in most Round One concrete tests; where slump either remained the same or decreased slightly (Figure 7.33). Water reducer (WR) was added at 454ml/100kg binder, as per the standard Holcim 30MPa Ultracem mix design. The only exception was the 30% Loesche (6k) mix, where slump reduced to 70mm, and cylinders were noticeably more difficult to finish. This was also the only Round One mix where the Loesche (6k) mix achieved a lower slump than Loesche (3k).

In Round Two, WR was initially added at 454ml/100kg binder, adding more as required to achieve a sufficiently workable mix (Figure 7.34). The addition of 5% Loesche (3k) pumice resulted in a clear improvement in workability, returning a slump of 120mm and easily finished concrete. This was not reflected in the addition of 5% Loesche (6k) pumice, where a clear reduction in workability was observed, and additional WR was required. Although it produced a final slump of 100mm, cylinders were still difficult to finish.

The 10% addition of both pumice samples again resulted in a clear reduction in workability, each returning 70mm slumps before the addition of extra water reducer. 15% and 30% mixes required further additional WR, with the 30% Loesche (6k) mix still only achieving a 70mm slump, although relatively easy to finish. Ultimately, to achieve target slump, blended mixes require higher WR dosages with increasing pumice addition, yet actual workability can vary quite substantially.

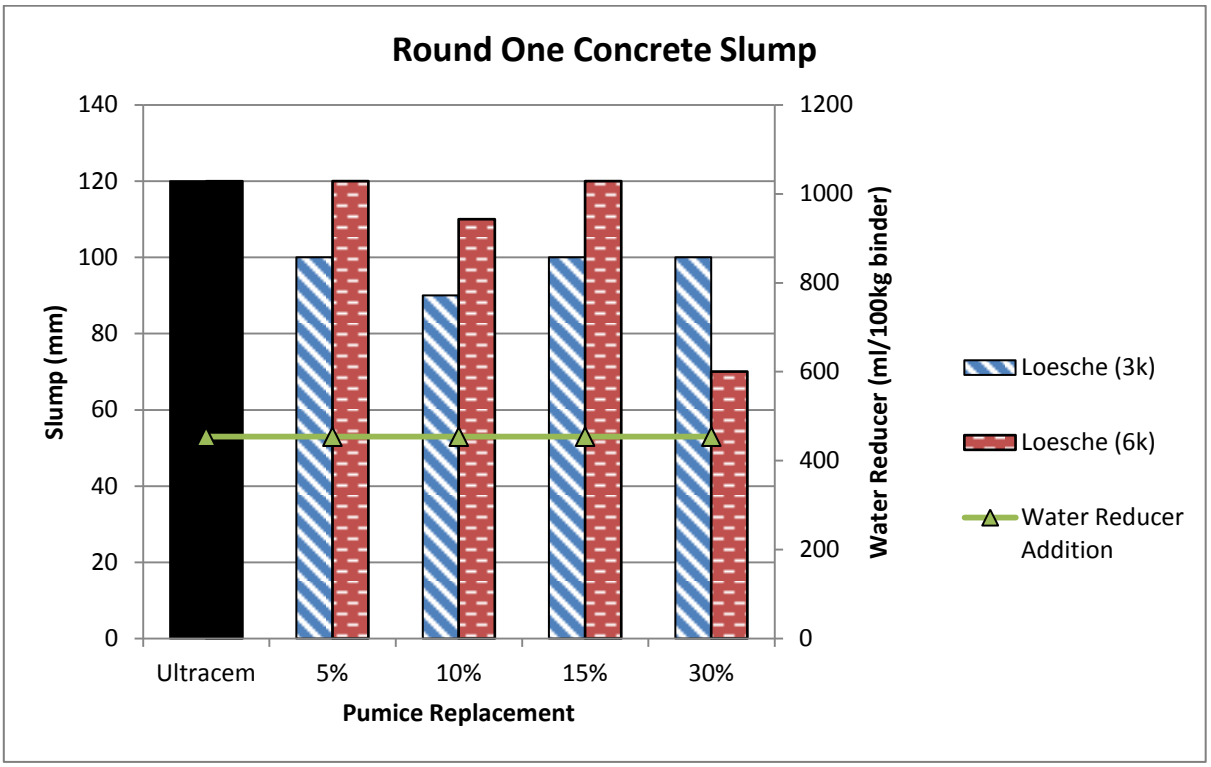

Figure 7.33: Round One concrete slump

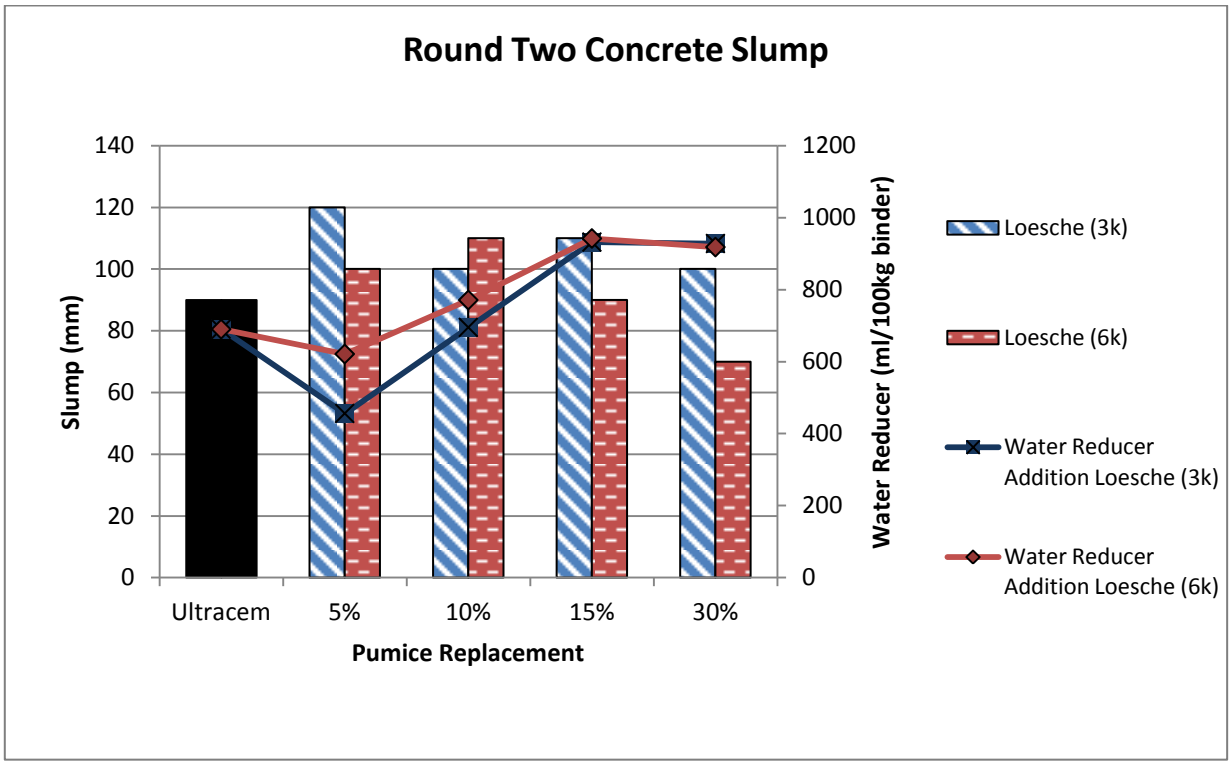

Figure 7.34: Round Two concrete slump

The high pH mix water used in Round Three appeared to have a negative effect on WR, resulting in a colour change upon addition, and reduced effectiveness (Figure 7.35). The high pH Reference mix returned a 70mm slump, although it remained sufficiently workable. As in Round Two, extra WR was added as required.

In Round Four, superplasticiser (SP) was added at a rate indicated by the manufacturer, then increased and reduced by 20% in respective mixes (Figure 7.36; Table 7.5). The intention of this round was to assess the effect of SP dosage rate on concrete strength; therefore workability and consistency were significantly affected.

As discussed in Section 7.5.3, each pumice sample behaved quite differently with the addition of superplasticiser (SP). The Loesche (6k) pumice required substantially higher SP dosages to achieve adequate workability. The effects of this were pronounced, and are reflected in slump results. This suggests differences in pumice adsorptive properties at different fineness, where the absorption of water, SP, or both are affected by the size of pumice grains. Regardless, even mixes with the lowest slump still provided adequately workable concrete for the purposes of this investigation.

Table 7.5: Round Four concrete slump

Mix Description	Slump (mm)
10% Loesche (3k) + SP (0.8)	40
10% Loesche (3k) + SP (1)	70
10% Loesche (3k) + SP (1.2)	70
10% Loesche (6k) + SP (0.8)	60
10% Loesche (6k) + SP (1)	70
10% Loesche (6k) + SP (1.2)	150

Slump results gained in these trials are in contrast with the improvements in workability recorded by Kaid et al., (2009) and Brown (1998). South (2009) however found a noticeable decrease in slump as the pumice substitution rate increased. This is thought to be due to the adsorption of water by the porous pumice structure, reducing the amount of free water available to enhance workability. While this is likely to be the active mechanism in reducing overall concrete slump in this thesis, the effects on actual workability vary. The commercial

use of this pozzolan will require more detailed analysis of blended concrete rheology, and pumice adsorptive properties.

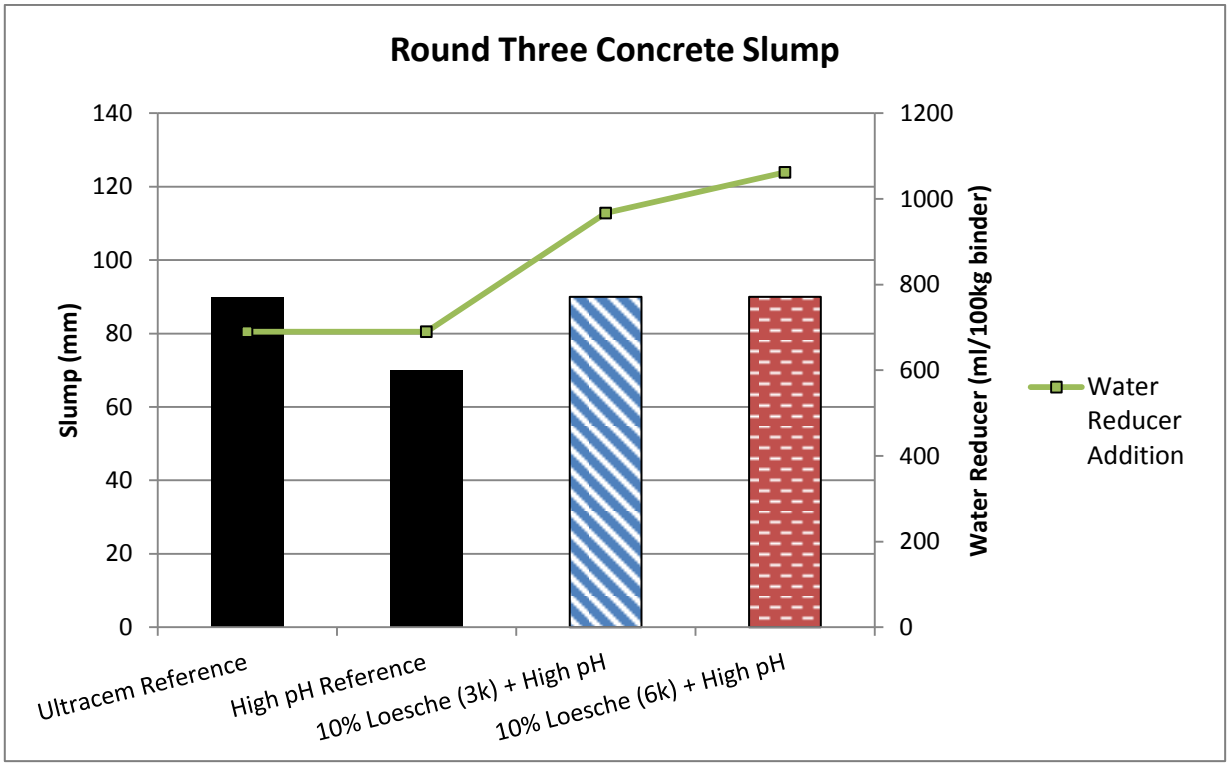

Figure 7.35: Round Three concrete slump

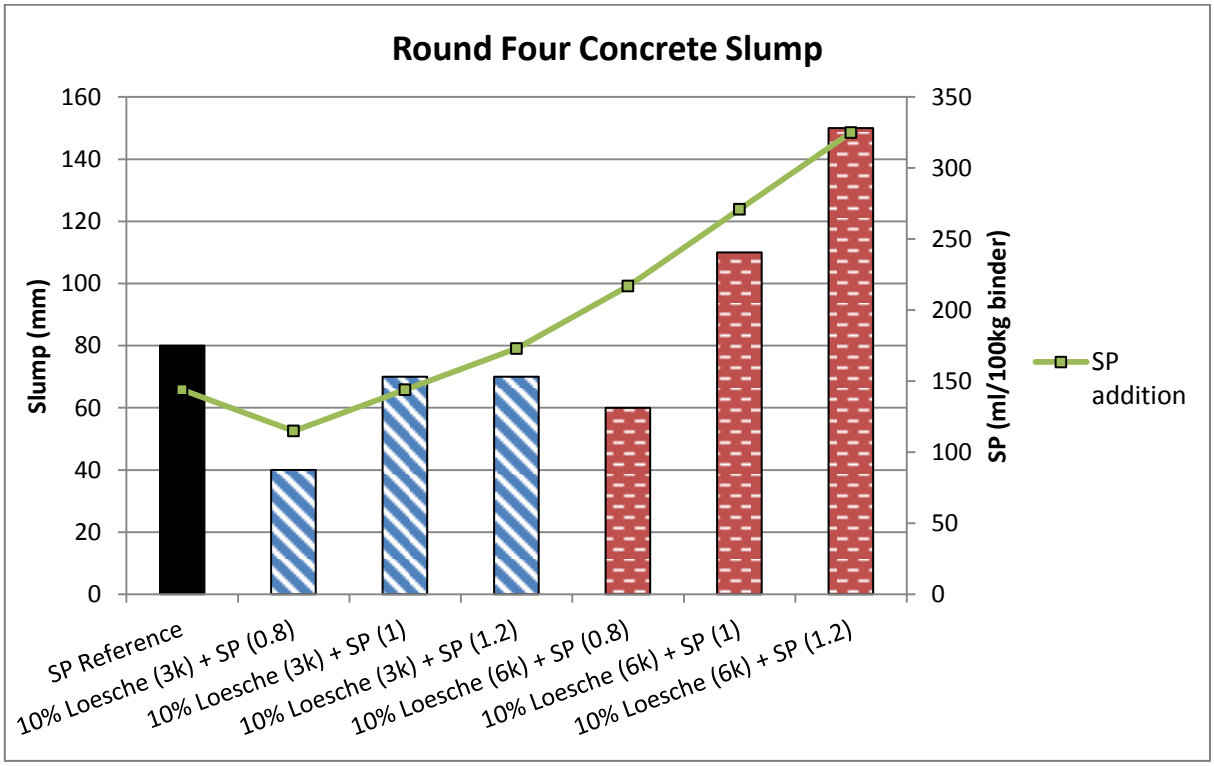

Figure 7.36: Round Four concrete slump

7.12 Air Entrainment

Air entrained concrete contains microscopic air bubbles which are distributed uniformly throughout the paste. Entrained air improves concrete workability, reduces bleeding and segregation, and improves the frost resistance of concrete. Entrained air can also significantly reduce concrete strength, and may result in increased strength variability (Caldarone, 2009).

In Round One, the addition of pumice has generally resulted in slight increases in air entrainment, with no distinctive trend between either pumice replacement rate or pumice fineness (Figure 7.37). With the reduction in w/b ratio, Round Two blended mixes generally show reductions in entrained air (Figure 7.38). Round Three shows essentially no variation (Figure 7.39), with all mixes returning very similar results to Ultracem.

In Round Four, both the SP reference and Loesche (6k) mixes show slight increases in entrained air relative to Ultracem. This may suggest that the substantially higher SP dose used in the Loesche (6k) mixes results in more entrained air. Even so, the subsequent increases and reductions in SP dose rates within each pumice sample have not had a noticeable influence on air entrainment (Figure 7.40).

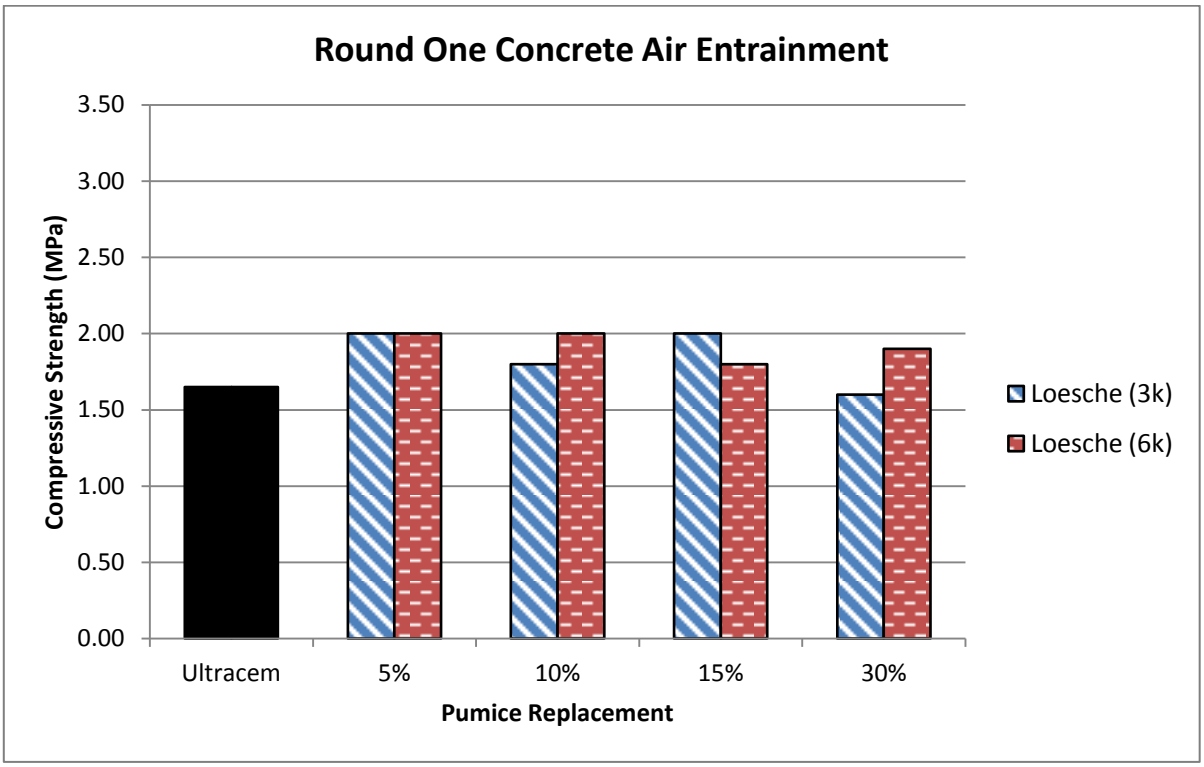

Figure 7.37: Round One concrete air entrainment

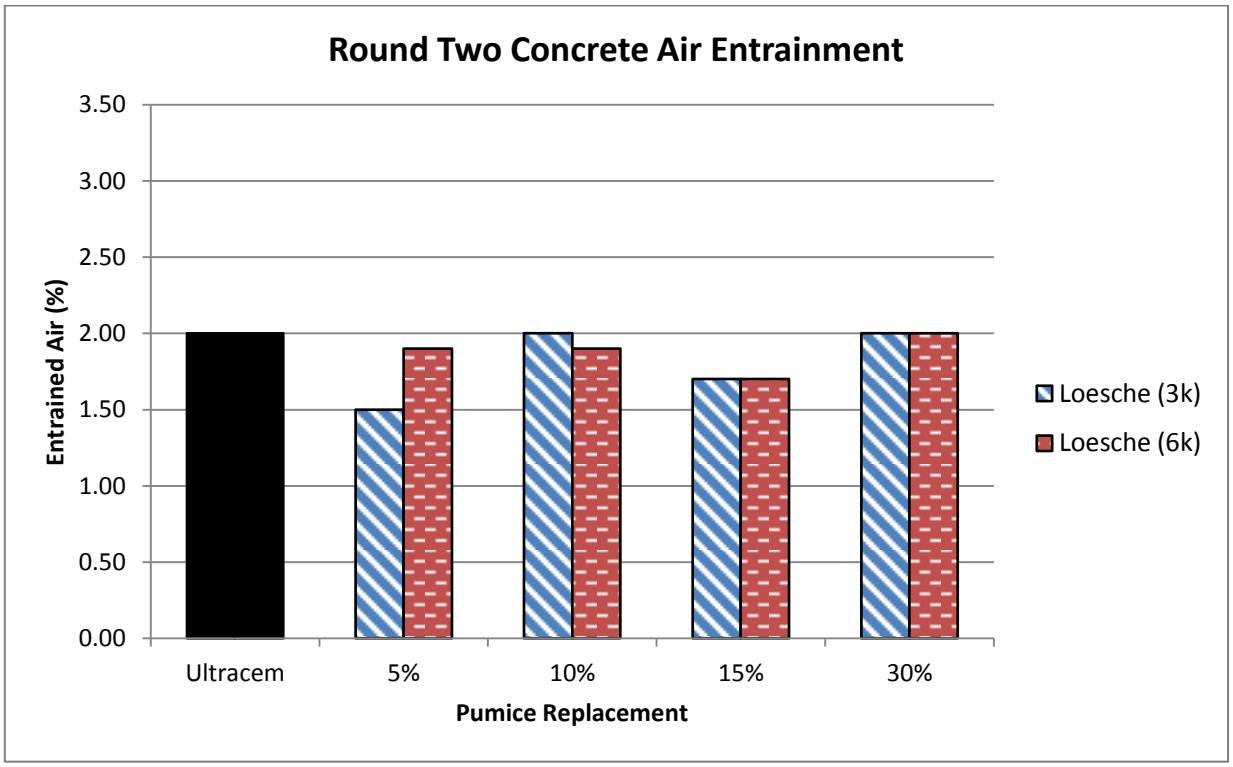

Figure 7.38: Round Two concrete air entrainment

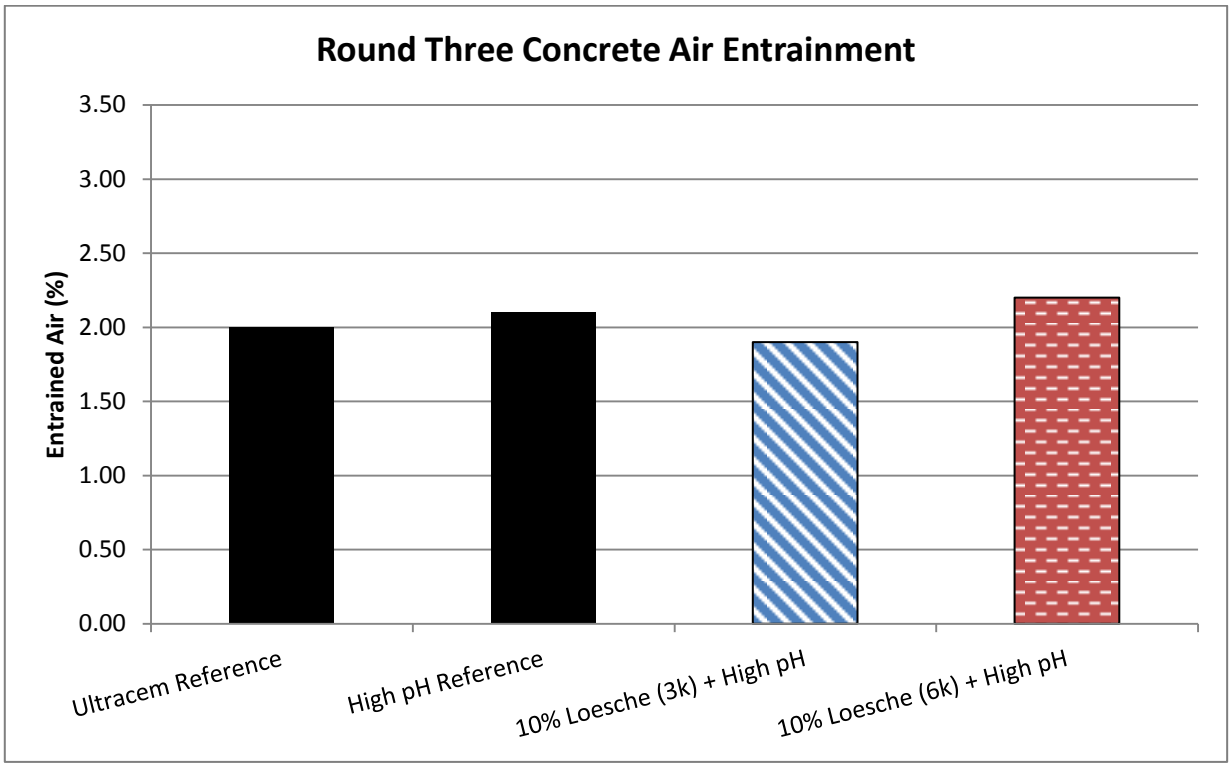

Figure 7.39: Round Three concrete air entrainment

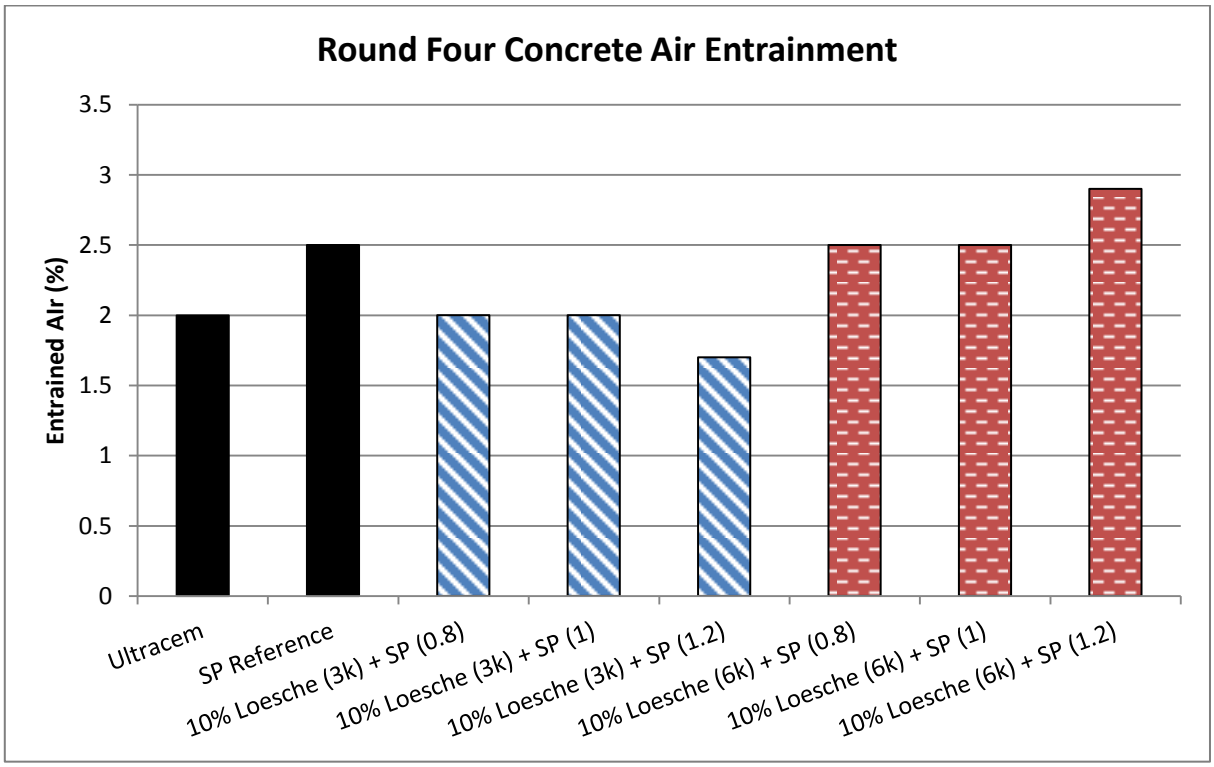

Figure 7.40: Round Four concrete air entrainment

Chapter 8 Conclusions

The objective of this study was to evaluate the effectiveness of Taupo Pumice from Rangiriri as a partial cement replacement in General Purpose Blended (GB) concrete. This is aimed at reducing cement CO_2 emissions and production costs through reduced clinker factor, while maintaining or enhancing concrete performance. Several aspects were considered, including concrete strength and durability, pumice chemistry and mineralogy, effects of particle fineness, and the use of concrete admixtures.

8.1 Concrete Strength

The partial replacement of cement with milled Taupo pumice invariably reduces concrete strength up to 28 days curing. Beyond this, blended concrete strength is much more promising, where of the 28 concrete mixes trialled, 14 achieved or surpassed 91 day Ultracem strength. Additionally, as 231 day durability tests show further improvements on 91 day results, concrete strength may also be expected to improve beyond 91 days.

Across all replacement levels, Round One (w/b=0.6) and Round Two (w/b=0.5) both returned mean 28 day strength reductions of 14%. Round One 91 day strengths were on average slightly higher than Ultracem, and Round Two strengths slightly below. Therefore, the reduction in w/b ratio had no effect on relative concrete strength at 28 days, and a slightly detrimental effect at 91 days.

Round Three tested the use of high pH mix water with 10% pumice, with average 28 day strengths 10% below Ultracem, and 91 day strengths slightly above. Round Four tested the use of superplasticiser (SP), presenting the most promising 28 day results of all mixes trialled. Average 28 day strengths were 8% below Ultracem, and 91 day strengths 3% above. This round also demonstrated the potential for further optimisation of SP dose rate, with the best result only 2% below Ultracem at 28 days.

8.2 Concrete Durability

The addition of pumice has resulted in significantly improved resistance to chloride ingress, especially at 30% replacement after extended curing. The finer Loesche (3k) pumice shows the greatest improvements relative to Ultracem. The addition of 10% pumice has shown moderate improvements in electrical resistivity, where substantial improvements are recorded with 30% pumice. The finer Loesche (3k) pumice is significantly more resistant than both the Loesche (6k) and Ultracem mixes. The addition of pumice has had little effect on concrete porosity, and while 10% pumice mixes show a moderate reduction at 91 days, Ultracem is still the least porous at 231 days.

8.3 Pumice Chemistry and Mineralogy

This pumice contains high percentages of amorphous glass and other pozzolanic compounds. It contains low percentages of deleterious materials (clays and organic carbon), and compares well with other pozzolans used throughout the world. Therefore, the composition of this pumice is considered favourable for use in blended concretes.

8.4 Effect of Pumice Fineness

In general, the finer pumice has produced better performing concrete than its coarser counterpart, and exhibits a lower water demand. Rounds One and Two generally showed good correlation between increased pumice fineness and increased strength. This trend was reversed in Round Three up to 28 days, suggesting the coarser pumice may react slightly quicker in the presence of high pH water.

In Round Four, the Loesche (3k) mix performs marginally better at 28 days, and substantially better at 91 days. Higher strength gains between 56-91 days are recorded, regardless of SP dose rate. The difference between pumice samples is likely due to a combination of reduced SSA and varying SP dose. The addition of both high pH water and superplasticiser has reduced the influence of pumice PSD or SSA on concrete strength at all ages, and optimisation of SP dose rate is expected to yield even higher concrete strengths.

8.5 Concluding Statement

Utilising materials such as Taupo Pumice has the potential to offer significant environmental and financial benefits to the New Zealand economy. With further study, market education, and improved regulation, substantial changes will be possible.

As pumice-cement concretes develop strength over a longer period of time, and early strength is generally impeded, 28 days may not be the most suitable age to assess concrete performance. Adjusting this would require major changes to New Zealand concrete specifications, and perhaps practical changes within the construction industry. NZS 3122 has already been adapted to allow the addition of 10% mineral limestone to GP cement, and while presenting challenges, this is now a standard product in the New Zealand market. Ultimately, if significant environmental and commercial outcomes are to be achieved, changes to these standards may become increasingly necessary.

While safety and quality can never be compromised, further study should still be directed at optimising regulations, construction practices, and the way in which cement and concrete is consumed. There is significant potential for use of this pumice in New Zealand concrete, ultimately producing a stronger, more durable, and more sustainable product.

Chapter 9 Recommendations

As this research progressed, several testing options and mix variations were considered. These were based on similar research conducted locally and internationally, as well as ideas developed during the course of this thesis. Potential commercial viability was considered in all mix designs, and none were attempted outside what could be reasonably achieved in an industrial setting.

This chapter is intended to give realistic testing recommendations in addition to those conducted. Variations are intentionally and inherently simple, requiring as little additional processing and plant as possible. Additionally, they aim to utilise materials which are either available locally, or easily acquired.

9.1 Site Investigation

To produce reliable, high quality concrete utilising a natural pozzolan, a fundamental knowledge of site geology, geochemistry and sedimentology is imperative. Detailed research into these parameters will benefit the holistic understanding of the material, and its performance in GB concrete.

The Rangiriri pumice deposit encompasses a wide range of grain sizes, ranging from silty sands to cobbles. Assessing the purity of pumice at various grainsizes may be considered as part of future research, specifically testing amorphous silica and calcium content (see Section 7.8.1), clays, and total organic compounds. Passing material through a screen prior to grinding may allow further material optimisation.

While it is likely that finer pumice is more heavily contaminated with deleterious materials, this research has shown that these are well within limits specified by international standards. Additionally, if the overall pumice particle size distribution was truncated to include only a specific range of grainsizes, mill efficiency could be affected (eg. larger clasts will require more energy to mill to a target fineness). Unless a specific range of particle

sizes exhibited significantly more favourable composition, there would appear to be little benefit in screening materials prior to milling.

Once this pumice is adequately proven through laboratory testing, spatial geological variations and groundwater conditions should be assessed in detail. This should incorporate new and existing borehole and test pit data, extensive XRD testing, and aquifer pump tests. Additionally, due to the high pumice moisture content (>40%), pumice stockpiles should be designed to remove as much moisture as possible through evaporation. This will reduce heat requirements in the milling process, further improving plant efficiency.

9.2 Fine Pumice 'Tail'

An early discussion with experts from Industrial Research Limited (IRL) suggested jet-milling an extremely fine pumice subsample to add to concrete in small amounts. This would add a fine 'tail' to the pumice PSD, and increase overall binder SSA. This could theoretically 'kick-start' the pozzolanic reaction, providing a boost to early concrete strength.

In practice, this would require a separate mill on site, and would add to both plant and processing costs. From a testing perspective, as marginal strength gains will likely diminish with increased fineness, optimising the PSD and SSA of the fine 'tail' will be important, as will optimising the amount in which to add.

Results have indicated that while pumice particle size does affect concrete strength and durability (particularly at later ages), the short term relationship is also influenced by other factors (see Section 7.5.2). Additionally, finer pumice used in this thesis required almost three times the amount of energy to mill. Optimal pumice fineness needs to be understood more thoroughly before any significant investment is made in further reducing particle size, and would require an entire suite of additional testing.

9.3 Gypsum Addition

Adding a small amount of milled gypsum has been suggested (South, 2009) as a way to boost early strength development. An optimal sulphate content will maximise cement performance, and is thought to be a function of clinker mineralogy, cement fineness and hydration time (South, 2009; Taylor, 1997).

South (2009) trialled cement-pumice mixes with 2, 3 and 4% additional sulphate. At 5, 10 and 20% pumice substitution rates, 28 day strengths were in each case improved by the addition of 2% sulphate (Figure 9.1). The viability of this option will depend not only on the outcomes of any additional material testing, but the results of economic feasibility studies.

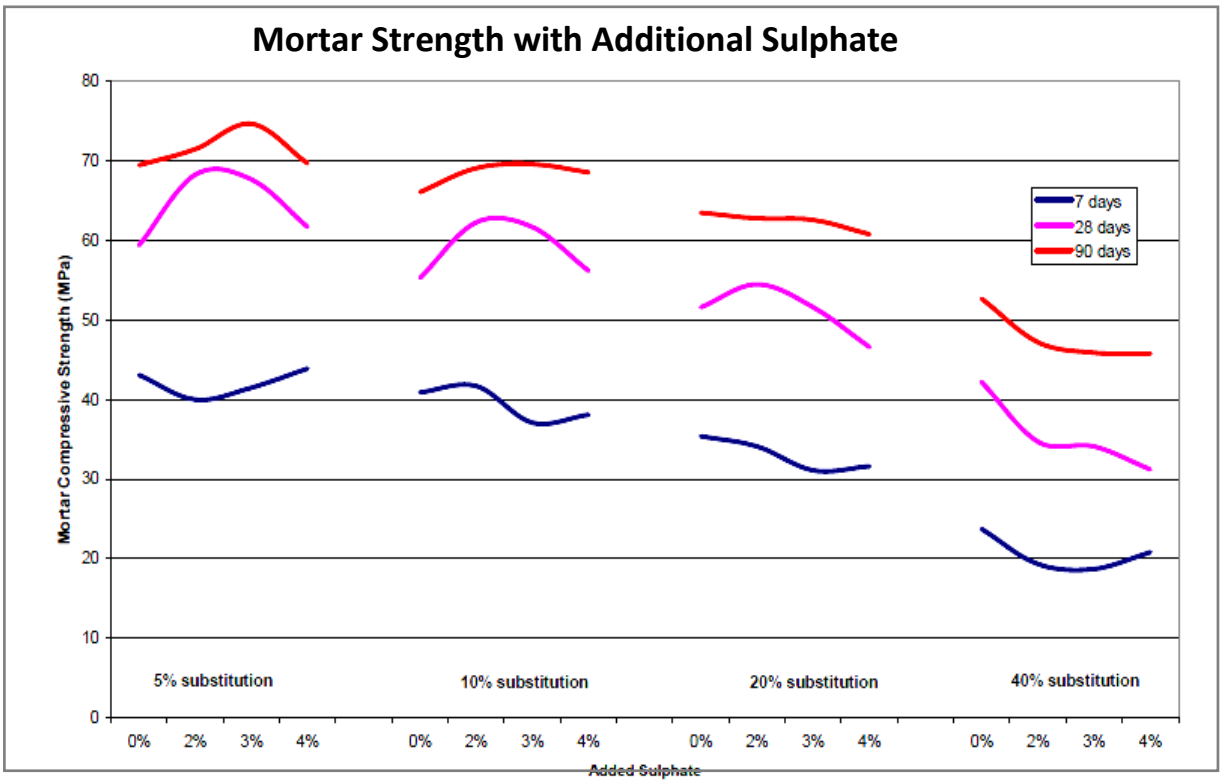

Figure 9.1: Mortar compressive strength with additional sulphate
(South, 2009)

9.4 Chemical Activators

Chemical activators present another avenue for testing, where additives such as sodium sulphate and calcium chloride have been found to enhance pozzolan reactivity (Shi & Day, 2001). While these could increase production costs, Shi & Day (2001) report that by using

this method, the marginal per unit concrete strength cost may actually decrease. Also, as chloride and sulphate ions are both deleterious to concrete durability, further long term analysis would be required.

If activators can be blended during milling, minimal additional plant will be required. However, the reactivity of these may be such that they need to be added at the batching plant, which may involve additional handling and compliance costs. The availability and cost of these activators will be limiting factors in this approach, and again, a full series of additional concrete tests will be required to determine optimal rates.

9.5 XRD-Rietveld Analysis

To further understand the chemical and mechanical interactions involving milled pumice in concrete, fast, reliable analysis of both crystalline and amorphous phases is critical. Rietveld analysis provides a means to utilise the speed and efficiency of XRD, while overcoming problems associated with peak overlap (see Section 2.6). Making concrete is relatively time consuming and labour intensive. If early concrete chemistry and mineralogy can be reliably correlated with strength and durability at later ages, there is potential to significantly reduce testing times, labour requirements and testing costs.

If XRD was proven as a reliable indicator of long term concrete strength and durability, the time between the conceptual phase and industrial output may be reduced, allowing greater research scopes. High quality chemical analyses will allow a more targeted approach to improving pozzolanic reactivity, where the effects on each strength forming phase can be isolated, understood, and enhanced, perhaps using specific activators or other suitable techniques.

9.6 Additional Microscopy

There is additional scope for improved understanding of blended pastes using both optical and scanning electron microscopy (SEM). Optical analysis of cement paste thin sections may give useful insight into the hydration of blended cements; however particular

expertise will be required to interpret these. SEM allows visual and geochemical analysis of materials at an extremely fine scale. This method was used to inspect each of the milled pumice samples used in this thesis (Section 5.4), and indeed provided a useful insight into the behaviour of the extremely fine particles. This method could be further utilised in understanding the hydration of the pumice-cement paste itself.

9.7 Superplasticiser Optimisation

As discussed in Section 7.5.3, there is scope to further optimise the use of superplasticiser (SP) in blended concretes, and explore the mechanisms of cement and pumice ζ-potential (see Section 7.10). This is likely to be affected by various SP types and dose rates, and understanding these relationships will contribute to SP optimisation, providing academically and commercially useful information.

The method used in Round Four should be repeated to understand the effectiveness of SP at higher pumice replacement levels, the effects of different types of SP, and the effects on mix ζ-potential. Additionally, it is possible that the interactions between cement, pumice and SP can themselves be optimised by adjusting pumice content, w/b ratio, solution pH, and pumice SSA. Clearly this would involve a substantial amount of additional testing, and the scope would need to be significantly refined.

9.8 Late Strength Development

Pumice-cement concretes have shown proportionally higher strength development between 28 and 91 days relative to Ultracem, especially with the use of the finer pumice. Testing concrete strengths at later ages, perhaps 180 days and older, will further establish the performance of composite blends after extended periods of time. This may be of particular importance in structures and designs which do not rely on early concrete strength for practical construction purposes.

9.9 Pozzolan Oversubstitution

Further testing possibilities lie in the oversubstitution of pozzolan, where pumice is added not only to replace an equivalent portion of cement, but a portion of sand as well. This effectively increases the overall binder content, and was tested by Brown (1998) using pumice from Horotiu (see Section 3.3). In doing this, concrete achieved (and in some cases exceeded) 28 day OPC reference strengths.

Unmilled pumice sand could be blended with milled pumice on site, adjusting batching plant mix designs accordingly; however this could prove complex and expensive. Feasibility will again rely on cost analyses, additional testing and the homogeneity of the unmilled pumice sand across the Rangiriri deposit.

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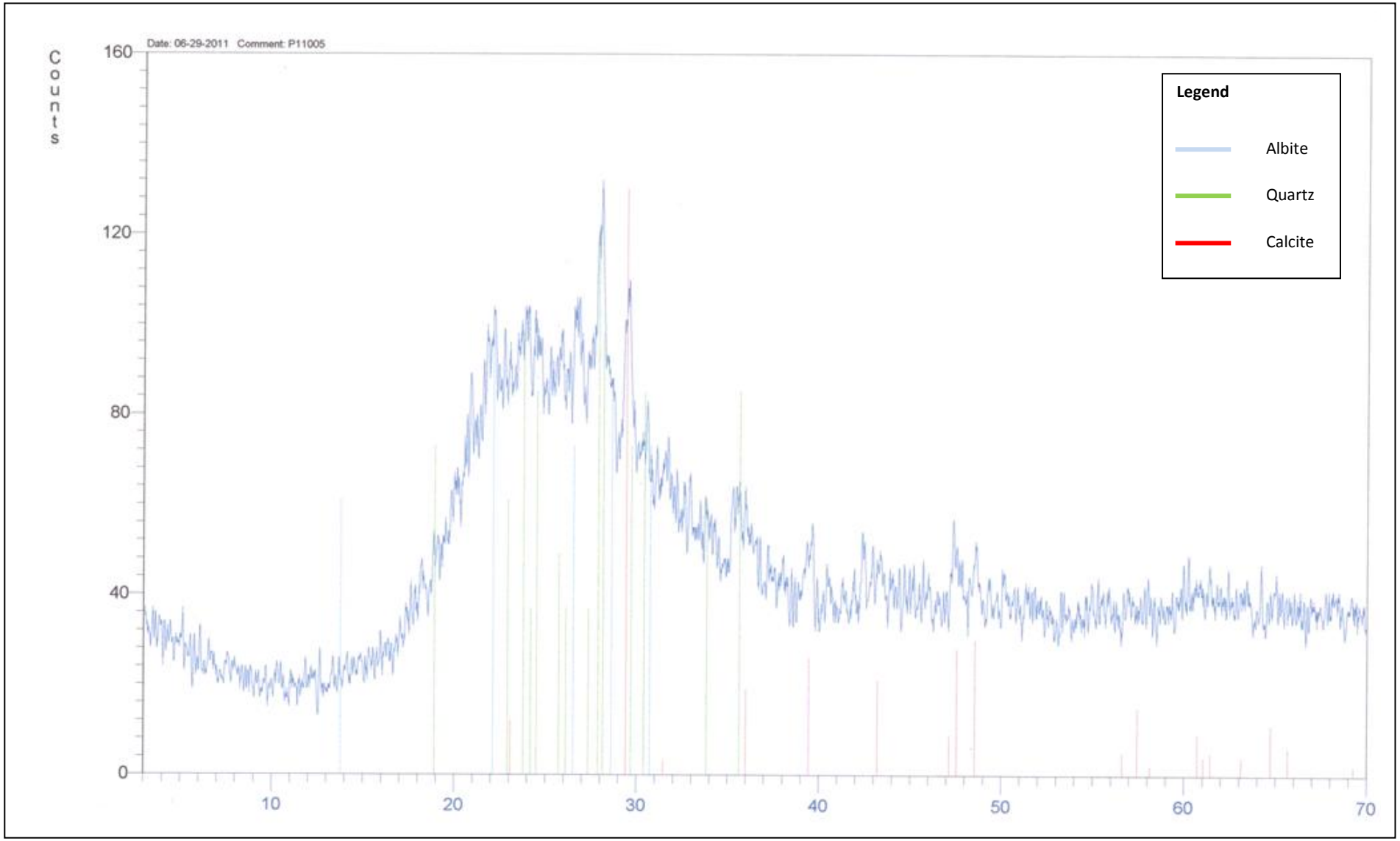
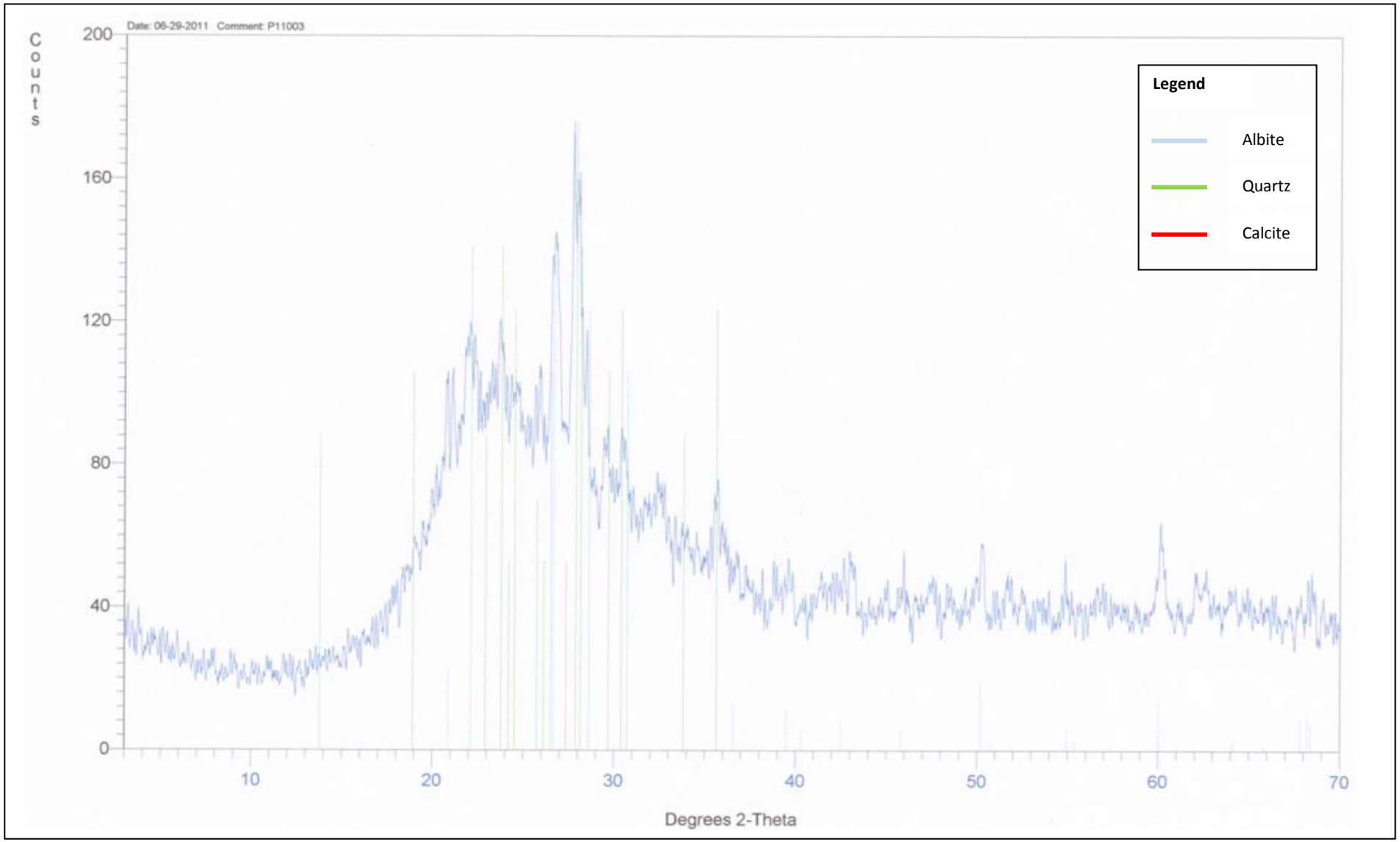
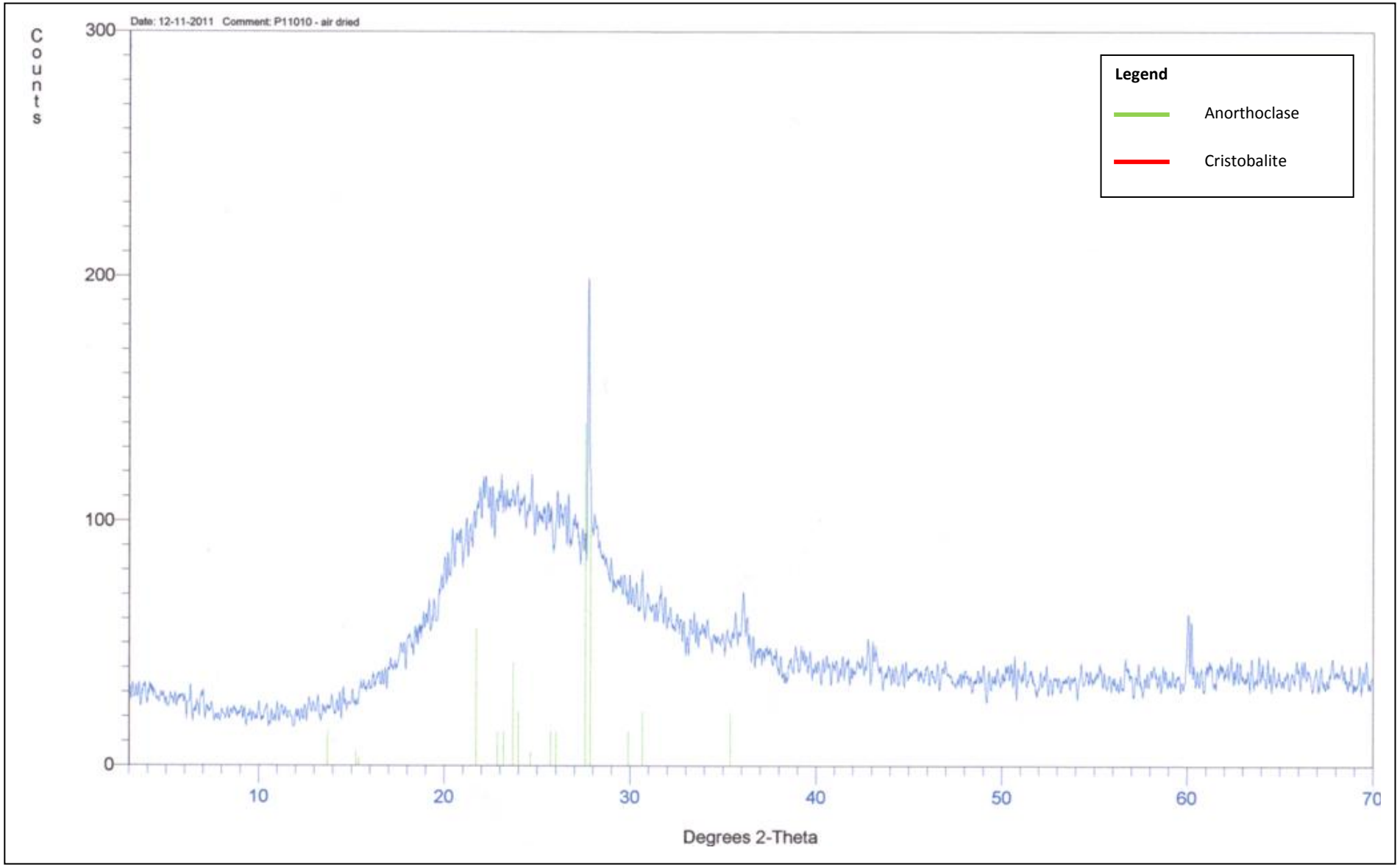
Appendix 1 Pumice XRD – Milled 'Horotiu Pumice'



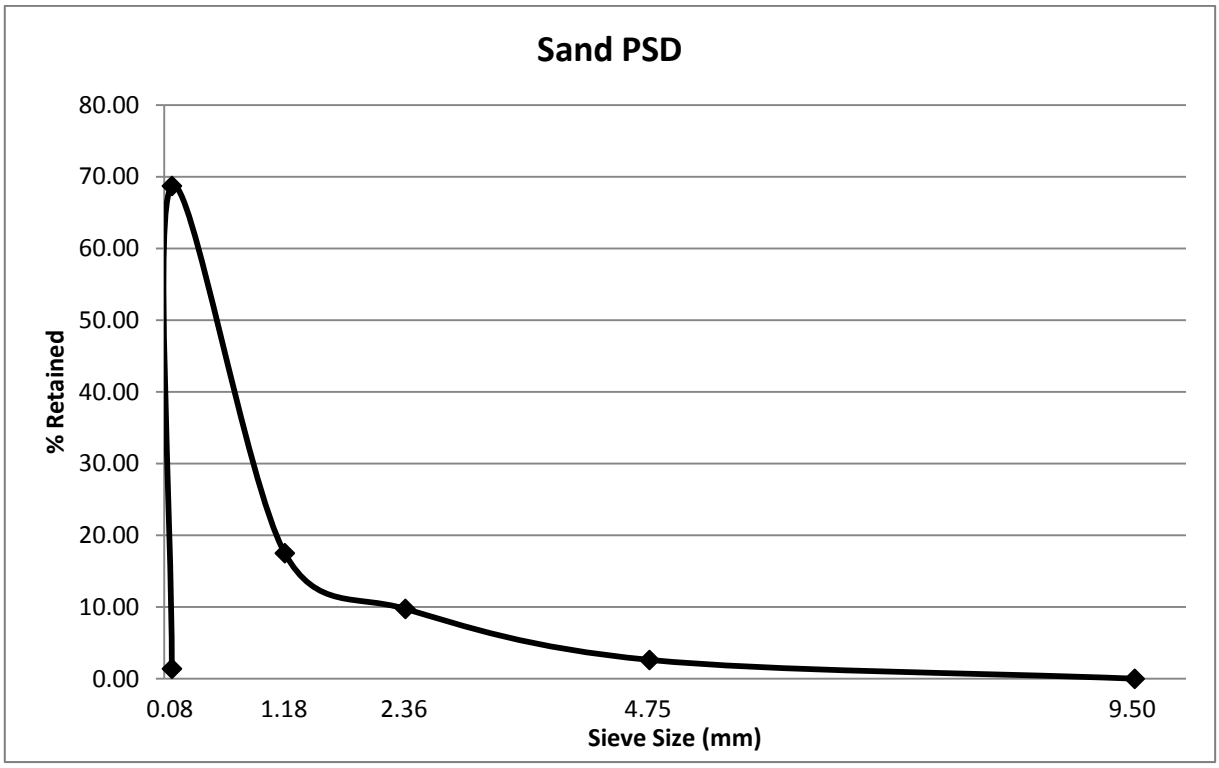
Appendix 2 Pumice XRD – Milled ‘Rangiriri Pumice’

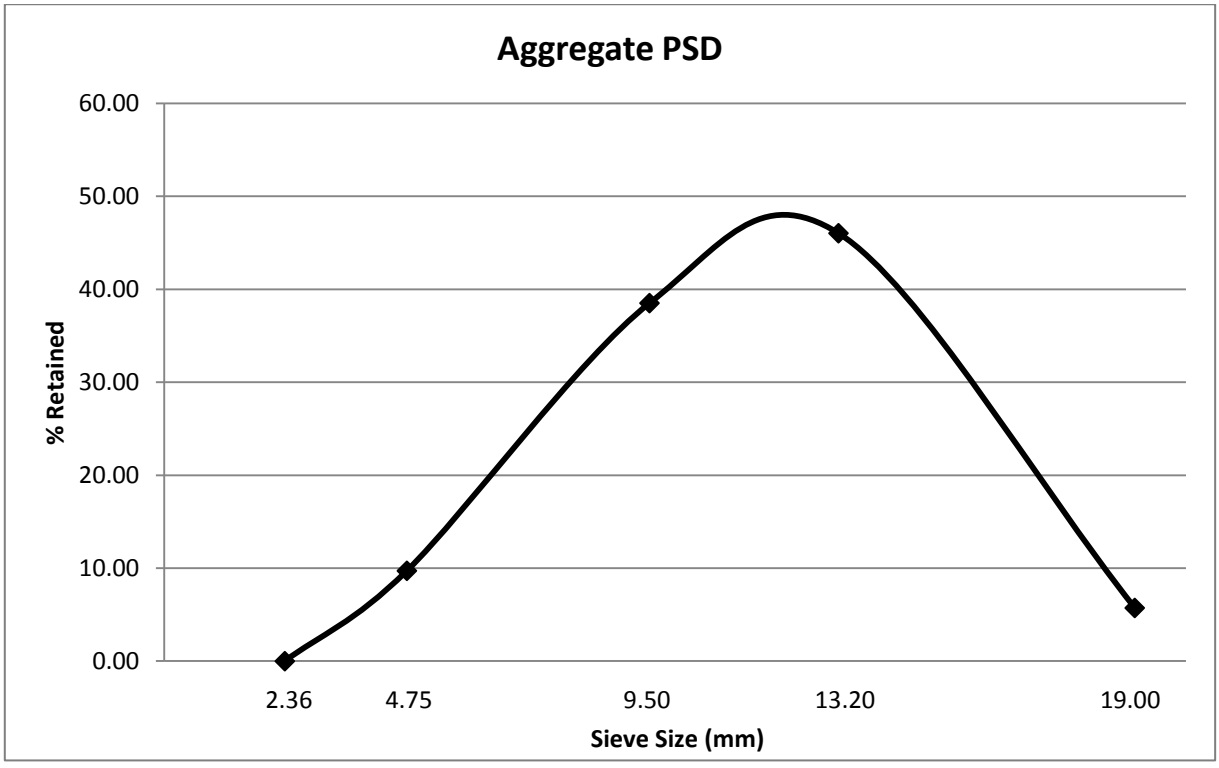


Appendix 3 Pumice XRD – Fresh 'Horotiu Pumice'



Appendix 4 Sand and Aggregate PSD





Appendix 5 Round One and Two Concrete Properties

	Age (days)	Date tested	Weight (g)	Avg. Diameter	Length (mm)	Tonnes Force	Factor	Mean Compression (MPa) (Rounded)	Slump (mm)	Entrained Air (%)
X10-152	3	14-Apr	3724.0	99.3	199.5	13.5	1.287	18.0	120	1.2
Round One Reference		14-Apr	3775.9	100.0	199.5	14.8	1.269			
	7	18-Apr	3788.3	100.1	200.5	20.4	1.266	26.5		
Date Made:		18-Apr	3779.5	100.0	200.5	21.5	1.269			
11/04/2011	28	9-May	3790.4	100.0	201.0	28.6	1.269	36.5		
		9-May	3772.0	100.0	200.5	28.6	1.269			
	91	11-Jul	3774.3	99.8	200.5	29.7	1.274	37.0		
		11-Jul	3783.5	99.9	200.4	28.0	1.271			
P11-018	3	14-Apr	3751.7	99.9	200.5	12.9	1.271	17.0	100	2.0
5% Loesche (3k)		14-Apr	3758.0	99.8	200.0	14.0	1.274			
	7	18-Apr	3777.6	100.0	200.5	19.5	1.269	24.5		
Date Made:		18-Apr	3751.5	99.9	200.5	18.9	1.271			
11/04/2011	28	9-May	3768.0	100.0	199.5	26.5	1.269	33.5		
		9-May	3779.6	100.1	200.0	26.5	1.266			
	91	11-Jul	3772.1	99.9	200.5	31.2	1.271	39.0		
		11-Jul	3779.2	100.0	200.3	30.0	1.269			
P11-019	3	14-Apr	3764.3	100.4	198.5	13.8	1.259	17.0	90	1.8
10% Loesche (3k)		14-Apr	3748.2	99.9	199.5	13.4	1.271			
	7	18-Apr	3744.2	100.3	200.0	19.4	1.261	24.5		
Date Made:		18-Apr	3760.0	100.2	199.5	19.1	1.264			
11/04/2011	28	9-May	3742.2	100.0	200.0	25.8	1.269	32.0		
		9-May	3749.2	100.1	200.0	24.8	1.266			
	91	11-Jul	3721.2	99.7	199.7	33.0	1.277	41.0		
		11-Jul	3764.7	100.0	200.5	31.8	1.269			

	Age (days)	Date tested	Weight (g)	Avg. Diameter	Length (mm)	Tonnes Force	Factor	Mean Compression (MPa) (Rounded)	Slump (mm)	Entrained Air (%)
P11-020	3	15-Apr	3753.9	100.4	199.0	11.7	1.259	14.5	100	2.0
15% Loesche (3k)		15-Apr	3763.9	100.2	199.5	11.6	1.264			
	7	19-Apr	3754.0	100.2	198.5	17.3	1.264	21.5		
Date Made:		19-Apr	3753.8	100.3	198.5	16.5	1.261			
12/04/2011	28	10-May	3781.4	100.0	199.7	24.5	1.269	30.5		
		10-May	3766.5	99.9	200.4	23.4	1.271			
	91	12-Jul	3790.0	100.1	200.4	31.7	1.266	40.0		
		12-Jul	3766.4	100.0	201.3	31.1	1.269			
P11-021	3	27-Apr	3773.0	100.0	200.0	7.1	1.269	9.0	100	1.6
30% Loesche (3k)		27-Apr	3745.0	99.9	200.5	7.1	1.271			
	7	1-May	3776.7	100.1	200.1	11.8	1.266	15.0		
Date Made:		1-May	3762.8	100.1	200.0	12.0	1.266			
24/04/2011	28	22-May	3701.0	100.0	199.5	19.7	1.269	25.0		
		22-May	3756.0	100.0	200.0	20.0	1.269			
	91	24-Jul	3744.0	100.1	199.0	28.0	1.266	35.0		
		24-Jul	3744.0	100.0	200.5	27.3	1.269			
P11-022	3	14-Apr	3784.8	100.2	200.0	11.9	1.264	15.5	120	2.0
5% Loesche (6k)		14-Apr	3767.8	100.0	200.0	12.2	1.269			
	7	18-Apr	3763.4	100.0	201.0	17.4	1.269	22.5		
Date Made:		18-Apr	3766.6	100.0	201.0	18.0	1.269			
11/04/2011	28	9-May	3724.4	99.7	200.0	23.0	1.277	30.5		
		9-May	3770.1	100.1	201.5	24.7	1.266			
	91	11-Jul	3761.7	100.0	200.3	27.6	1.269	35.0		
		11-Jul	3763.4	100.0	200.2	27.6	1.269			

	Age (days)	Date tested	Weight (g)	Diameter - right angles (mm)		Avg. Diameter	Length (mm)	Tonnes Force	Factor	Mean Compression (MPa) (Rounded)	Slump (mm)	Entrained Air (%)
P11-023	3	15-Apr	3762.9	99.9	100.0	100.0	201.0	11.0	1.269	14.0	110	2.0
10% Loesche (6k)		15-Apr	3753.2	99.6	99.6	99.6	200.0	11.0	1.279			
	7	19-Apr	3766.5	100.0	100.0	100.0	200.0	17.7	1.269	22.0		
Date Made:		19-Apr	3778.2	100.0	100.1	100.1	199.0	17.3	1.266			
12/04/2011	28	10-May	3745.7	99.9	99.9	99.9	200.1	24.2	1.271	30.5		
		10-May	3782.8	100.2	100.0	100.1	199.8	23.6	1.266			
	91	12-Jul	3773.9	99.9	99.9	99.9	200.1	30.0	1.271	37.5		
		12-Jul	3773.0	99.9	100.1	100.0	199.7	29.3	1.269			
P11-024	3	27-Apr	3747.0	99.9	99.9	99.9	199.5	10.7	1.271	13.5	120	1.8
15% Loesche (6k)		27-Apr	3772.0	100.0	100.1	100.1	200.0	10.4	1.266			
	7	1-May	3770.9	99.9	100.0	100.0	200.5	16.1	1.269	20.5		
Date Made:		1-May	3781.7	100.1	100.0	100.1	200.0	16.3	1.266			
24/04/2011	28	22-May	3774.0	100.0	100.0	100.0	200.0	22.5	1.269	28.0		
		22-May	3729.0	100.0	100.0	100.0	200.0	21.5	1.269			
	91	24-Jul	3703.0	100.0	100.0	100.0	200.0	27.7	1.269	35.0		
		24-Jul	3771.0	100.1	1000.1	550.1	200.5	27.2	1.266			
P11-025	3	27-Apr	3736.0	99.8	99.8	99.8	199.0	6.6	1.274	8.5	70	1.9
30% Loesche (6k)		27-Apr	3737.0	99.9	100.0	100.0	200.0	6.9	1.269			
	7	1-May	3733.3	99.9	99.9	99.9	200.1	9.1	1.271	11.5		
Date Made:		1-May	3712.0	100.0	100.0	100.0	199.9	9.3	1.269			
24/04/2011	28	22-May	3720.0	100.0	100.0	100.0	199.5	18.6	1.269	23.0		
		22-May	3725.0	100.0	100.0	100.0	200.5	18.0	1.269			
	91	24-Jul	3745.0	100.1	100.2	100.2	200.0	25.3	1.264	32.5		
		24-Jul	3735.0	100.2	100.2	100.2	199.5	25.9	1.264			

	Age (days)	Date tested	Weight (g)	Diameter - right angles (mm)		Avg. Diameter	Length (mm)	Tonnes Force	Factor	Mean Compression (MPa) (Rounded)	Slump (mm)	Entrained Air (%)
P11-027	3	9-Jun	3793.4	99.7	99.8	99.8	200.5	24.5	1.274	31.5	90	2.0
Round Two Reference		9-Jun	3762.9	99.7	99.7	99.7	200.0	25.0	1.277			
	7	13-Jun	3798.4	99.9	100.1	100.0	201.0	32.5	1.269	41.0		
Date Made:		13-Jun	3742.4	99.3	99.4	99.4	201.0	31.8	1.284			
6/06/2011	28	4-Jul	3783.6	100.0	99.9	100.0	199.9	39.1	1.269	49.5		
		4-Jul	3798.4	99.8	100.0	99.9	200.6	39.1	1.271			
	91	5-Sep	3816.4	100.1	100.1	100.1	201.0	39.9	1.266	52.5		
		5-Sep	3808.5	100.2	100.2	100.2	200.0	43.0	1.264			
P11-028	3	9-Jun	3774.4	100.0	100.1	100.1	200.5	20.0	1.266	24.5	120	1.5
5% Loesche (3k) (2)		9-Jun	3772.8	99.9	99.9	99.9	200.0	18.4	1.271			
	7	13-Jun	3769.0	100.0	100.0	100.0	200.0	26.5	1.269	34.5		
Date Made:		13-Jun	3774.8	100.0	100.0	100.0	200.0	27.9	1.269			
6/06/2011	28	4-Jul	3782.1	100.0	100.0	100.0	200.3	32.5	1.269	41.0		
		4-Jul	3761.7	100.0	100.0	100.0	200.0	32.0	1.269			
	91	5-Sep	3766.9	100.1	100.1	100.1	200.0	37.6	1.266	48.5		
		5-Sep	3799.6	100.1	100.2	100.2	200.0	38.7	1.264			
P11-029	3	9-Jun	3775.2	100.1	100.0	100.1	199.0	21.0	1.266	27.0	100	2.0
10% Loesche (3k) (2)		9-Jun	3790.3	100.3	100.3	100.3	200.5	21.5	1.261			
	7	13-Jun	3770.9	100.4	99.8	100.1	199.0	28.0	1.266	35.5		
Date Made:		13-Jun	3773.5	99.8	99.9	99.9	200.0	28.3	1.271			
6/06/2011	28	4-Jul	3773.0	100.3	100.3	100.3	200.0	36.0	1.261	44.0		
		4-Jul	3766.4	99.8	99.8	99.8	200.4	33.8	1.274			
	91	5-Sep	3774.7	100.1	100.4	100.3	198.5	41.0	1.261	52.0		
		5-Sep	3814.4	100.0	100.4	100.2	200.0	41.1	1.264			

	Age (days)	Date tested	Weight (g)	Diameter - right angles (mm)		Avg. Diameter	Length (mm)	Tonnes Force	Factor	Mean Compression (MPa) (Rounded)	Slump (mm)	Entrained Air (%)
P11-030	3	26-Jun		100.7	100.3	100.5	201.0	20.1	1.256	25.5	110	1.7
15% Loesche (3k) (2)		26-Jun		99.9	99.7	99.8	199.5	20.0	1.274			
	7	30-Jun		100.1	100.2	100.2	200.0	26.6	1.264	33.5		
Date Made:		30-Jun		100.2	100.6	100.4	199.5	26.6	1.259			
23/06/2011	28	21-Jul		99.7	99.9	99.8	200.0	31.9	1.274	41.5		
		21-Jul		99.8	99.9	99.9	199.5	33.6	1.271			
	91	22-Sep		100.1	100.3	100.2	200.0	45.0	1.264	56.0		
		22-Sep		99.8	100.1	100.0	199.5	43.8	1.269			
P11-031	3	26-Jun		99.5	99.4	99.5	200.5	14.0	1.282	18.5	100	2.0
30% Loesche (3k) (2)		26-Jun		100.3	100.4	100.4	200.0	15.5	1.259			
	7	30-Jun		99.8	100.0	99.9	200.5	20.8	1.271	27.0		
Date Made:		30-Jun		100.1	100.1	100.1	200.0	22.1	1.266			
23/06/2011	28	21-Jul		99.8	99.9	99.9	200.5	30.5	1.271	38.5		
		21-Jul		99.9	100.0	100.0	200.0	30.5	1.269			
	91	22-Sep		99.8	99.9	99.9	200.0	37.6	1.271	46.5		
		22-Sep		100.0	100.1	100.1	200.0	35.8	1.266			
P11-032	3	9-Jun	3802.6	100.0.	100.1	100.1	200.0	22.2	1.266	28.0	100	1.9
5% Loesche (6k) (2)		9-Jun	3797.6	100.0	100.0	100.0	201.0	21.9	1.269			
	7	13-Jun	3792.3	99.7	99.8	99.8	200.0	30.5	1.274	38.5		
Date Made:		13-Jun	3797.2	100.0	100.1	100.1	200.0	30.5	1.266			
6/06/2011	28	4-Jul	3773.4	99.8	99.9	99.9	200.5	36.1	1.271	45.5		
		4-Jul	3802.9	100.0	100.1	100.1	199.6	35.4	1.266			
	91	5-Sep	3774.2	100.0	100.0	100.0	201.0	40.0	1.269	50.5		
		5-Sep	3795.9	100.0	100.1	100.1	200.5	39.6	1.266			

	Age (days)	Date tested	Weight (g)	Diameter - right angles (mm)		Avg. Diameter	Length (mm)	Tonnes Force	Factor	Mean Compression (MPa) (Rounded)	Slump (mm)	Entrained Air (%)
P11-033	3	9-Jun	3823.4	100.2	100.6	100.4	200.5	20.3	1.259	25.5	110	1.9
10% Loesche (6k) (2)		9-Jun	3790.5	100.0	100.1	100.1	201.5	20.2	1.266			
	7	13-Jun	3845.3	100.1	100.3	100.2	203.0	26.6	1.264	34.0		
Date Made:		13-Jun	3851.9	100.5	100.6	100.6	202.5	27.5	1.254			
6/06/2011	28	4-Jul	3820.8	100.2	100.5	100.4	202.0	31.5	1.259	41.5		
		4-Jul	3826.9	100.2	100.6	100.4	200.4	34.3	1.259			
	91	5-Sep	3766.0	100.1	99.8	100.0	199.0	38.6	1.282	49.5		
		5-Sep	3777.1	100.1	100.4	100.3	198.5	39.3	1.261			
P11-034	3	26-Jun		99.7	99.8	99.8	200.0	19.8	1.274	25.5	90	1.7
15% Loesche (6k) (2)		26-Jun		100.2	100.2	100.2	198.5	20.0	1.264			
	7	30-Jun		99.9	100.0	100.0	200.0	27.1	1.269	33.5		
Date Made:		30-Jun		100.2	100.3	100.3	198.5	26.0	1.261			
23/06/2011	28	21-Jul		100.2	100.3	100.3	198.0	31.6	1.261	41.0		
		21-Jul		99.9	99.9	99.9	199.5	33.0	1.271			
	91	22-Sep		100.1	100.3	100.2	199.0	39.7	1.264	49.5		
		22-Sep		100.1	100.3	100.2	199.0	38.9	1.264			
P11-035	3	26-Jun		100.2	100.2	100.2	200.0	14.4	1.264	18.0	70	2.0
30% Loesche (6k) (2)		26-Jun		100.3	100.3	100.3	200.0	14.0	1.261			
	7	30-Jun		99.9	100.2	100.1	200.5	19.3	1.264	24.0		
Date Made:		30-Jun		100.3	100.5	100.4	201.0	19.0	1.259			
23/06/2011	28	21-Jul		100.0	100.0	100.0	200.0	25.5	1.269	32.0		
		21-Jul		100.3	100.4	100.4	201.0	25.0	1.259			
	91	22-Sep		99.9	100.2	100.1	200.6	33.0	1.266	42.0		
		22-Sep		100.0	100.0	100.0	200.2	33.2	1.269			

Appendix 6 Round Three and Four Concrete Properties

	Age (days)	Date tested	Weight (g)	Diameter - right angles (mm)		Avg. Diameter	Length (mm)	Tonnes Force	Factor	Mean Compression (MPa) (Rounded)	Slump (mm)	Entrained Air (%)
P11-046	3	31-Aug	3805.0	100.0	100	100.0	200.0	26.4	1.269	33.5	70	2.1
		31-Aug	3822.4	100.0	100.1	100.1	200.0	26.2	1.266			
High pH Reference	7	4-Sep	3794.4	99.9	99.9	99.9	200.0	33.2	1.271	42.5		
		4-Sep	3812.0	100.0	100.1	100.1	200.5	33.9	1.266			
Date Made:	28	25-Sep	3812.2	100.0	100	100.0	200.5	37.2	1.269	49.0		
28/08/2011		25-Sep	3800.4	100.2	100.1	100.2	201.0	40.0	1.264			
	56	23-Oct	3807.8	100.0	100.1	100.1	200.6	41.0	1.266	53.5		
		23-Oct	3790.4	99.8	99.8	99.8	199.8	43.3	1.274			
	91	27-Nov	3804.2	100.1	100.1	100.1	201.1	43.6	1.266	55.0		
		27-Nov	3759.5	99.2	99.9	99.9	200.2	43.1	1.287			
P11-047	3	31-Aug	3867.2	100.2	100.5	100.4	201.5	23.5	1.259	29.5	90	1.9
		31-Aug	3832.0	100.3	100.5	100.4	199.5	23.6	1.259			
High pH + 10% Loesche (3k)	7	4-Sep	3855.6	100.3	100.5	100.4	202.0	29.0	1.259	37.5		
		4-Sep	3832.7	100.3	100.4	100.4	200.5	30.6	1.259			
Date Made:	28	25-Sep	3854.0	100.5	100.4	100.5	201.5	36.0	1.256	44.0		
28/08/2011		25-Sep	3850.5	100.3	100.7	100.5	200.5	34.4	1.256			
	56	23-Oct	3843.0	100.2	100.4	100.3	200.3	41.0	1.261	52.5		
		23-Oct	3855.6	100.3	100.4	100.4	201.7	42.0	1.259			
	91	27-Nov	3879.0	100.3	100.4	100.4	201.7	42.0	1.259	54.5		
		27-Nov	3838.1	100.2	100.5	100.4	201.0	44.4	1.259			

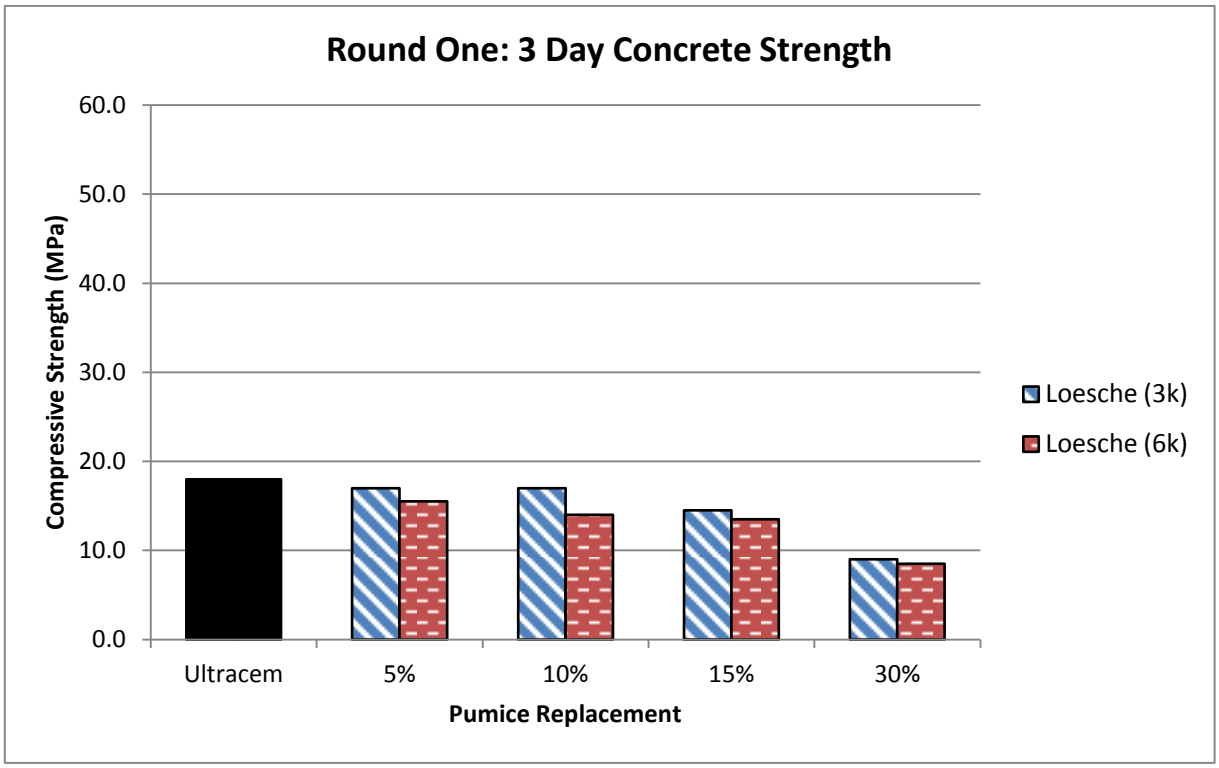
	Age (days)	Date tested	Weight (g)	Diameter - right angles (mm)		Avg. Diameter	Length (mm)	Tonnes Force	Factor	Mean Compression (MPa) (Rounded)	Slump (mm)	Entrained Air (%)
P11-048	3	31-Aug	3799.6	99.9	100.1	100.0	200.5	23.5	1.269	30.0	90	2.2
		31-Aug	3817.9	100.1	100.1	100.1	201.0	24.2	1.266			
High pH + 10% Loesche (6k)	7	4-Sep	3803.4	99.9	100	100.0	200.5	29.8	1.269	38.0		
		4-Sep	3812.4	100.1	100.1	100.1	201.0	30.4	1.266			
Date Made:	28	25-Sep	3794.3	100.0	100.1	100.1	200.0	35.0	1.266	45.5		
28/08/2011		25-Sep	3805.4	100.1	100.3	100.2	200.5	36.7	1.264			
	56	23-Oct	3794.0	100.0	99.9	100.0	200.2	41.0	1.269	52.5		
		23-Oct	3788.3	100.0	100.1	100.1	199.5	42.0	1.266			
	91	27-Nov	3790.8	100.0	100.1	100.1	199.5	42.0	1.266	53.5		
		27-Nov	3800.8	100.2	100.1	100.2	200.0	42.4	1.264			
P11-049	3	1-Sep	3835.5	100.2	100.5	100.4	202.0	24.0	1.259	30.0	80	2.5
		1-Sep	3843.6	100.3	100.5	100.4	202.0	23.5	1.259			
Ref SP	7	5-Sep	3843.6	100.6	100.5	100.6	202.5	31.8	1.254	39.5		
		5-Sep	3825.1	100.5	100.4	100.5	200.5	30.9	1.256			
Date Made:	28	26-Sep	3810.4	100.4	100.4	100.4	201.5	36.0	1.259	45.5		
29/08/2011		26-Sep	3780.9	100.5	100.6	100.6	200.0	36.3	1.254			
	56	24-Oct	3841.0	100.3	100.5	100.4	202.4	39.8	1.259	50.0		
		24-Oct	3815.6	100.2	100.6	100.4	201.5	39.6	1.259			
	91	28-Nov	3839.3	100.4	100.7	100.6	201.0	43.0	1.254	53.5		
		28-Nov	3844.6	100.5	100.3	100.4	202.0	42.5	1.259			

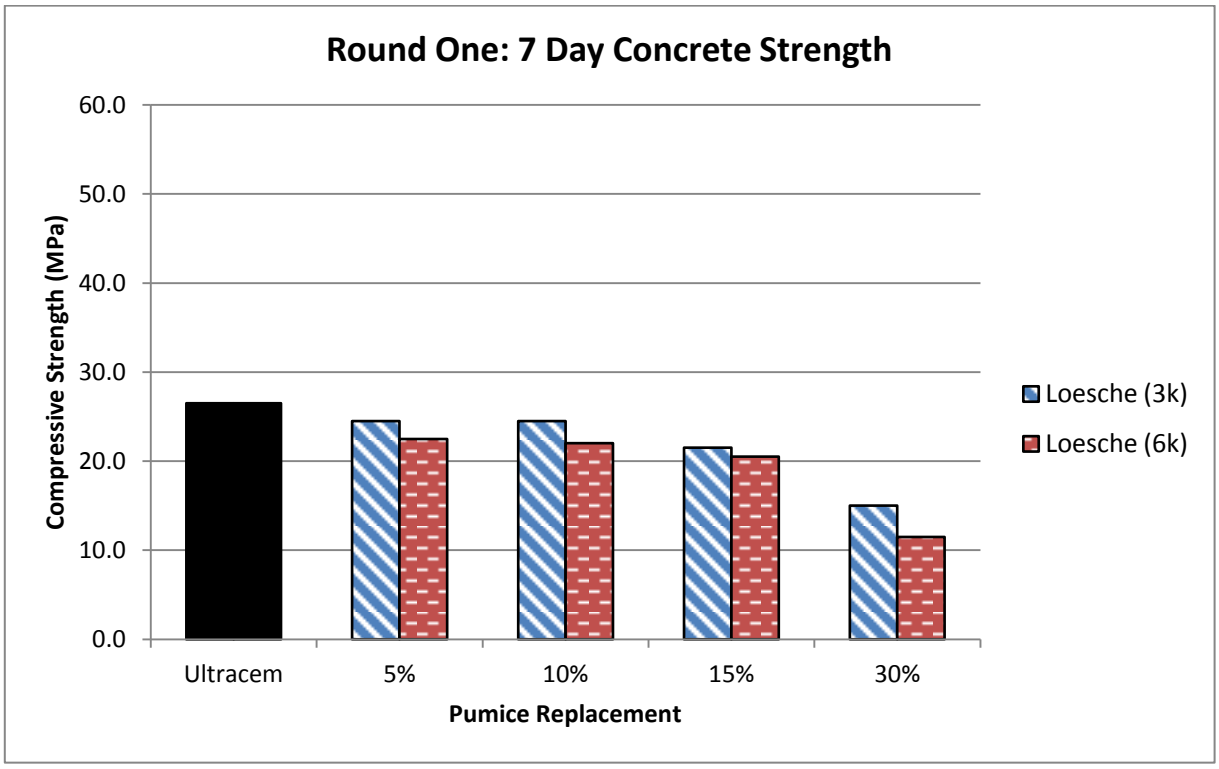
	Age (days)	Date tested	Weight (g)	Diameter - right angles (mm)		Avg. Diameter	Length (mm)	Tonnes Force	Factor	Mean Compression (MPa) (Rounded)	Slump (mm)	Entrained Air (%)
P11-050	3	1-Sep	3730.3	99.2	99.4	99.3	199.5	21.8	1.269	28.0	70	2.0
		1-Sep	3779.9	100.0	100.1	100.1	199.0	21.6	1.287			
SP + 10% Loesche (3k) (1)	7	5-Sep	3787.2	100.0	100	100.0	201.0	29.0	1.269	37.0		
		5-Sep	3781.1	100.1	100.1	100.1	200.0	29.5	1.266			
Date Made:	28	26-Sep	3798.8	100.2	100.3	100.3	201.0	36.1	1.261	45.0		
29/08/2011		26-Sep	3790.0	100.1	100.1	100.1	200.0	35.0	1.266			
	56	24-Oct	3777.1	99.9	100.1	100.0	199.5	39.4	1.269	51.0		
		24-Oct	3768.6	100.2	99.8	100.0	200.3	41.0	1.269			
	91	28-Nov	3795.4	99.9	100.1	100.0	201.5	45.3	1.269	56.5		
		28-Nov	3791.4	99.9	100.0	100.0	201.5	43.6	1.269			
P11-051	3	12-Sep	3842	100.3	100.5	100.4	200.5	23.0	1.259	28.0	110	2.5
		12-Sep	3803	100.3	100.5	100.4	200.2	22.8	1.259			
SP + 10% Loesche (6k) (1)	7	16-Sep	3856.0	100.3	100.4	100.4	201.5	31.1	1.259	39.0		
		16-Sep	3849.2	100.3	100.4	100.4	202.0	30.6	1.259			
Date Made:	28	7-Oct	3849.7	100.3	100.5	100.4	203.2	36.7	1.259	46.0		
9/09/2011		7-Oct	3843.6	100.3	100.4	100.4	200.6	36.3	1.259			
	56	4-Nov	3859.9	100.3	100.5	100.4	202.5	41.0	1.259	51.0		
		4-Nov	3836.1	100.3	100.5	100.4	201.5	40.4	1.259			
	91	9-Dec	3844.8	100.7	100.2	100.5	201.5	43.7	1.231	53.0		
		9-Dec	3845.9	100.5	100.4	100.5	201.5	42.7	1.231			

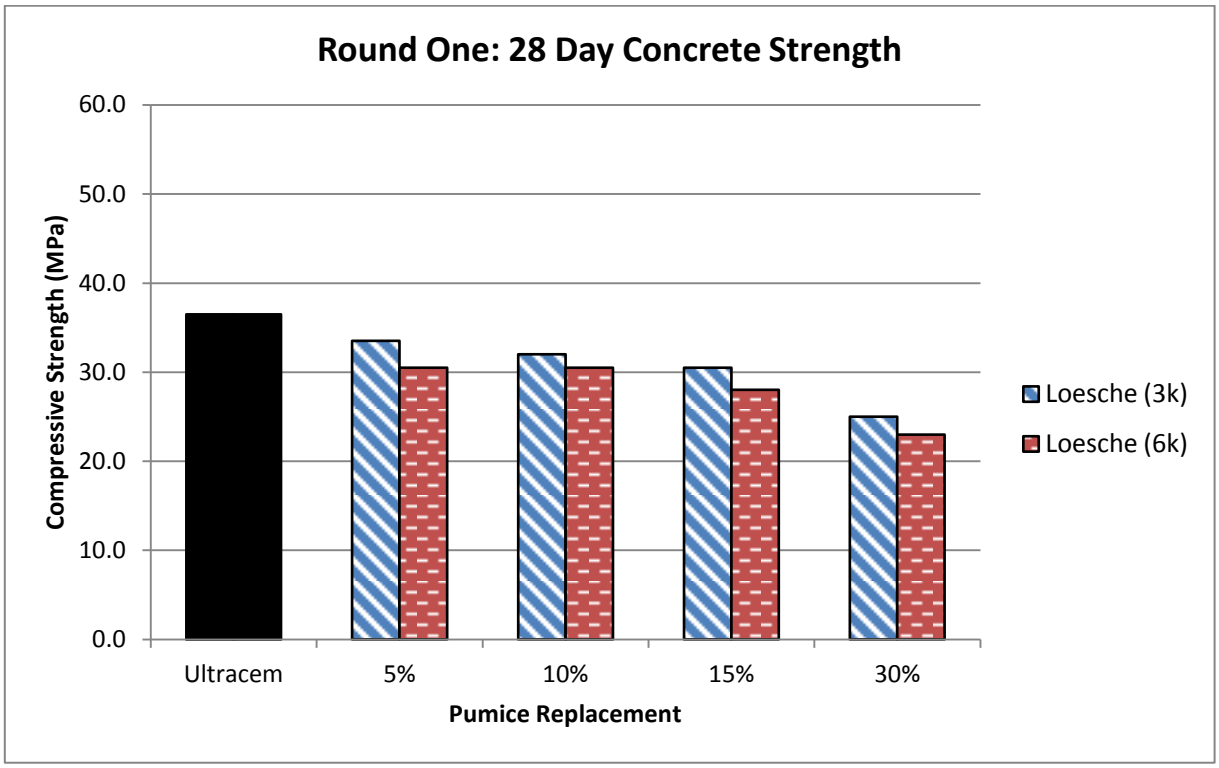
	Age (days)	Date tested	Weight (g)	Diameter - right angles (mm)		Avg. Diameter	Length (mm)	Tonnes Force	Factor	Mean Compression (MPa) (Rounded)	Slump (mm)	Entrained Air (%)
P11-052	3	12-Sep	3811.1	100.1	100.1	100.1	201.0	23.4	1.266	29.5	40	2.0
		12-Sep	3838.6	100.2	100.2	100.2	201.5	23.4	1.264			
SP + 10% Loesche (3k) (0.8)	7	16-Sep	3837.3	100.4	100.3	100.4	201.0	28.8	1.259	37.5		
		16-Sep	3844.5	100.3	100.4	100.4	201.5	31.0	1.259			
Date Made:	28	7-Oct	3806.7	100.2	100.5	100.4	200.0	38.3	1.259	48.5		
9/09/2011		7-Oct	3848.9	100.2	100.4	100.3	201.9	38.6	1.261			
	56	4-Nov	3836.8	100.6	100.4	100.5	200.5	40.7	1.231	50.5		
		4-Nov	3833.6	100.5	100.4	100.5	200.5	41.2	1.231			
	91	9-Dec	3851.2	100.3	100.6	100.6	201.5	45.6	1.231	54.0		
		9-Dec	3830.8	100.4	100.5	100.5	202.0	42.0	1.231			
P11-053	3	12-Sep	3773.4	99.9	99.9	99.9	200.0	21.2	1.271	27.0	60	2.5
		12-Sep	3776.6	99.8	100.0	99.9	200.5	21.5	1.269			
SP + 10% Loesche (6k) (0.8)	7	16-Sep	3785.1	99.8	99.8	99.8	201.5	28.3	1.274	36.0		
		16-Sep	3790.9	100.0	100.0	100.0	200.0	28.1	1.269			
Date Made:	28	7-Oct	3764.0	100.1	100.1	100.1	201.0	34.0	1.266	44.0		
9/09/2011		7-Oct	3795.1	100.1	100.0	100.1	200.3	35.5	1.269			
	56	4-Nov	3771.5	100.2	100.3	100.3	200.5	39.8	1.261	49.5		
		4-Nov	3776.5	100.2	100.1	100.2	200.0	38.6	1.264			
	91	9-Dec	3767.5	99.9	99.8	99.9	200.5	41.4	1.271	52.5		
		9-Dec	3774.3	99.9	99.8	99.9	200.5	41.5	1.271			

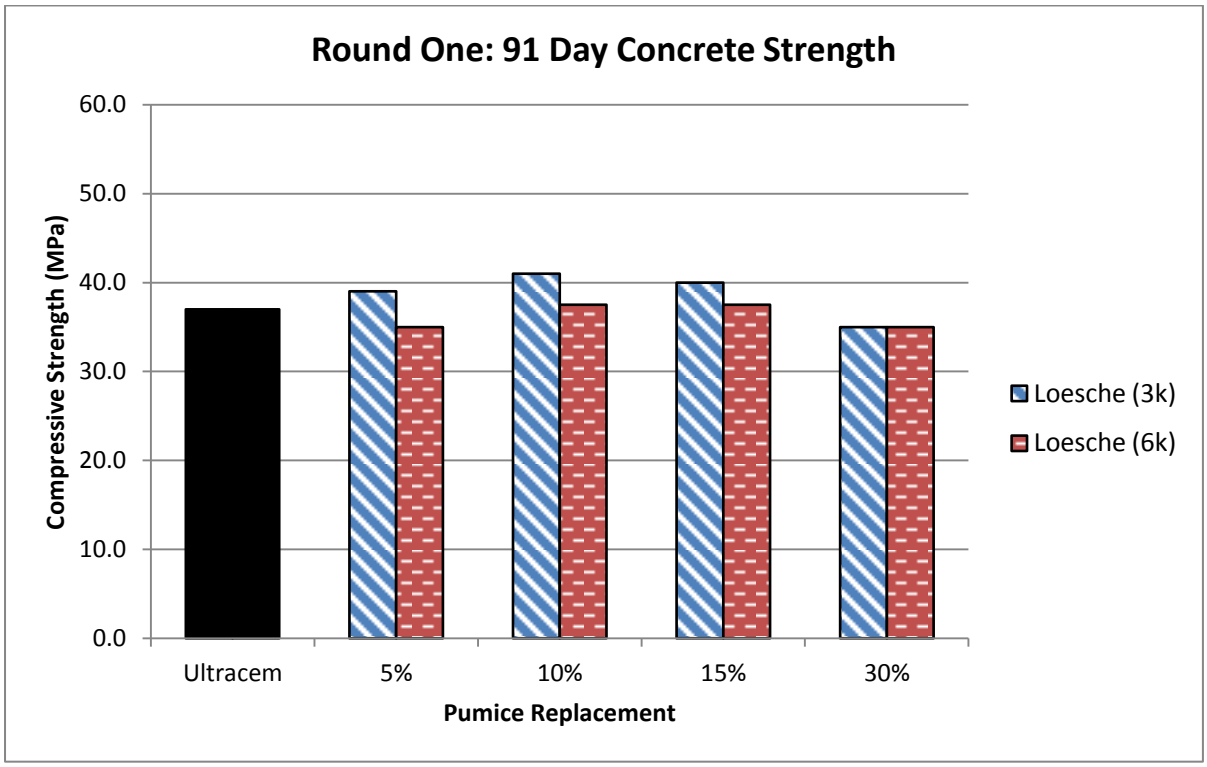
	Age (days)	Date tested	Weight (g)	Diameter - right angles (mm)		Avg. Diameter	Length (mm)	Tonnes Force	Factor	Mean Compression (MPa) (Rounded)	Slump (mm)	Entrained Air (%)
P11-054	3	12-Sep	3790.1	100.0	100	100.0	200.0	22.6	1.269	28.5	70	1.7
		12-Sep	3793.6	100.0	100	100.0	202.0	22.3	1.269			
SP + 10% Loesche (3k) (1.2)	7	16-Sep	3729.6	99.2	99.4	99.3	201.5	29.1	1.287	37.5		
		16-Sep	3795.6	100.1	99.9	100.0	200.0	30.6	1.269			
Date Made:	28	7-Oct	3788.7	99.9	100.1	100.0	200.3	34.6	1.269	44.0		
9/09/2011		7-Oct	3807.8	100.1	99.9	100.0	200.5	37.1	1.269			
	56	4-Nov	3769.4	99.8	99.5	99.7	201.0	39.5	1.277	50.5		
		4-Nov	3814.3	100.1	100.2	100.2	201.0	40.7	1.264			
	91	9-Dec	3780.4	99.9	99.9	99.9	200.5	44.7	1.269	56.5		
		9-Dec	3792.0	100.2	100.2	100.2	200.0	45.1	1.264			
P11-055	3	12-Sep	3785.3	99.9	100	100.0	200.0	21.5	1.269	27.5	150	2.9
		12-Sep	3765.6	99.9	100.2	100.1	200.0	22.0	1.266			
SP + 10% Loesche (6k) (1.2)	7	16-Sep	3754.1	99.9	100	100.0	200.0	29.1	1.269	37.0		
		16-Sep	3774.0	100.0	100.2	100.1	200.1	29.4	1.266			
Date Made:	28	7-Oct	3771.5	99.9	99.7	99.8	200.8	35.2	1.274	44.5		
9/09/2011		7-Oct	3748.2	99.9	99.7	99.8	199.8	35.0	1.274			
	56	4-Nov	3790.5	100.3	100.4	100.4	200.5	39.1	1.259	50.0		
		4-Nov	3783.3	100.0	100.0	100.0	200.0	40.0	1.269			
	91	9-Dec	3774.6	99.9	100.1	100.0	200.5	39.1	1.259	0.2		
		9-Dec	3801.0	100.0	100.1	100.1	200.0	40.0	1.269			

Appendix 7 Round One Concrete Strength

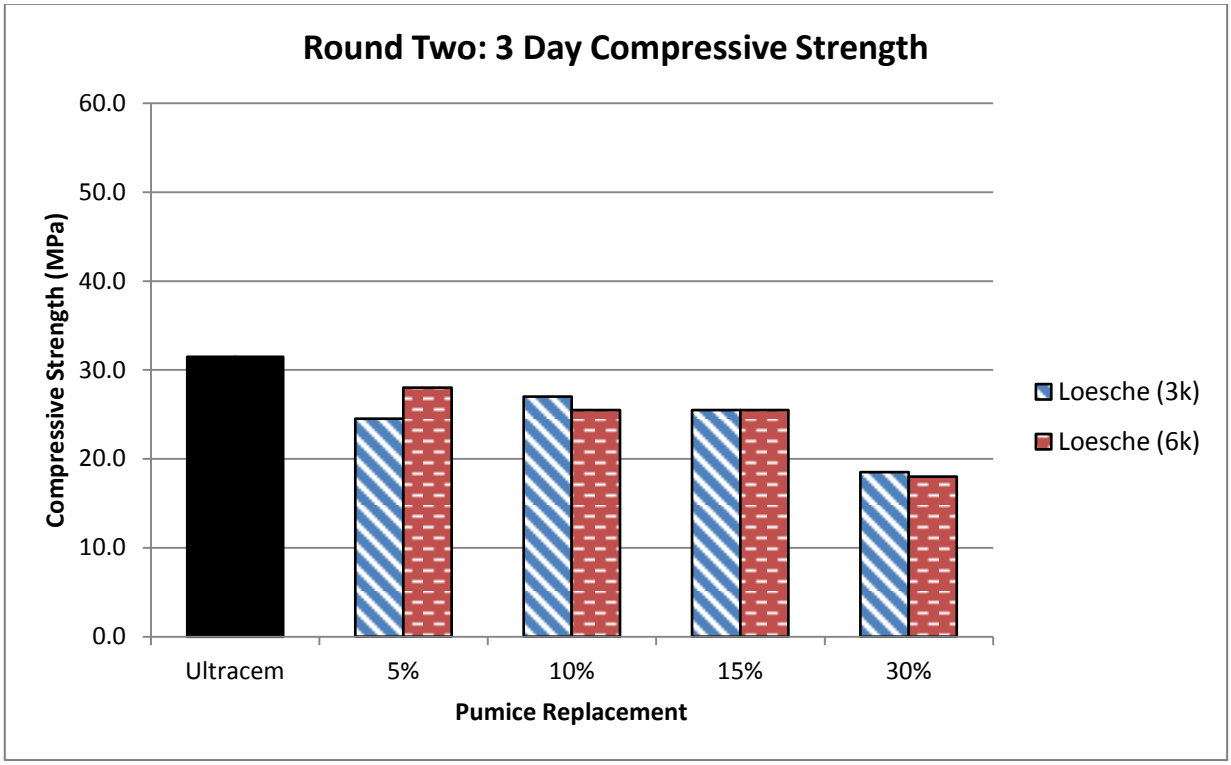


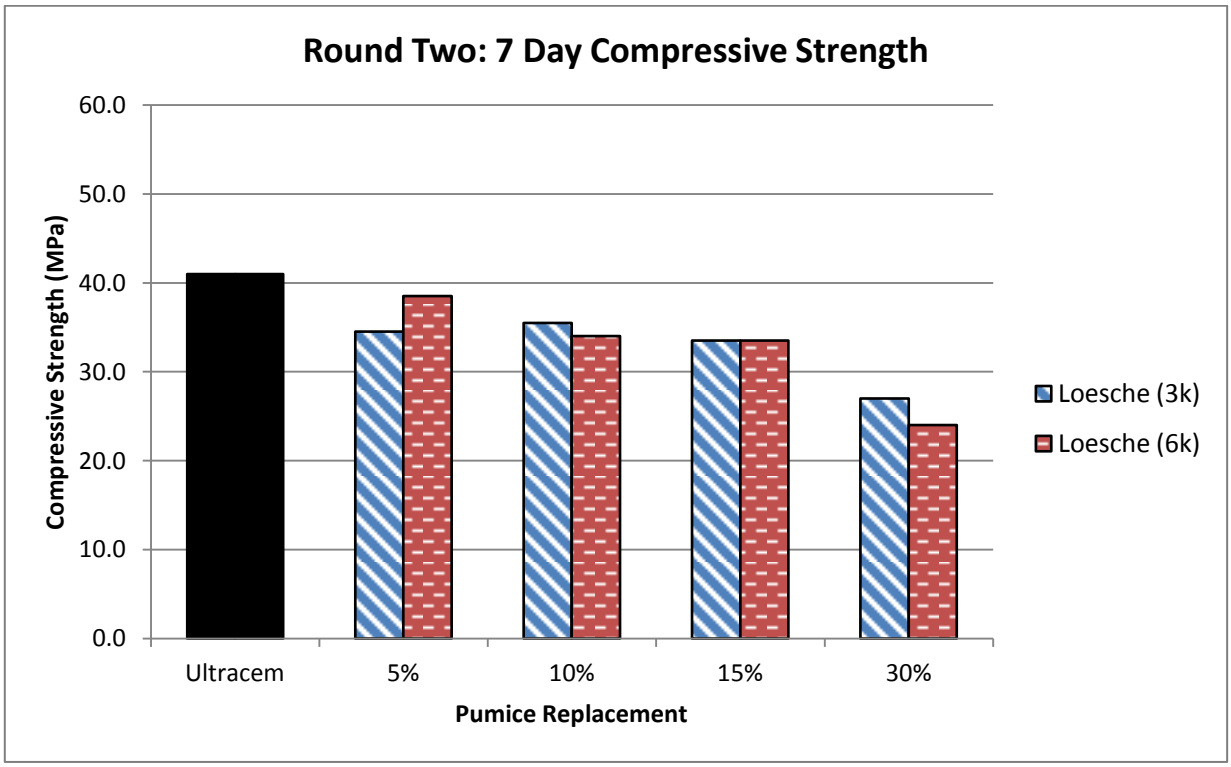


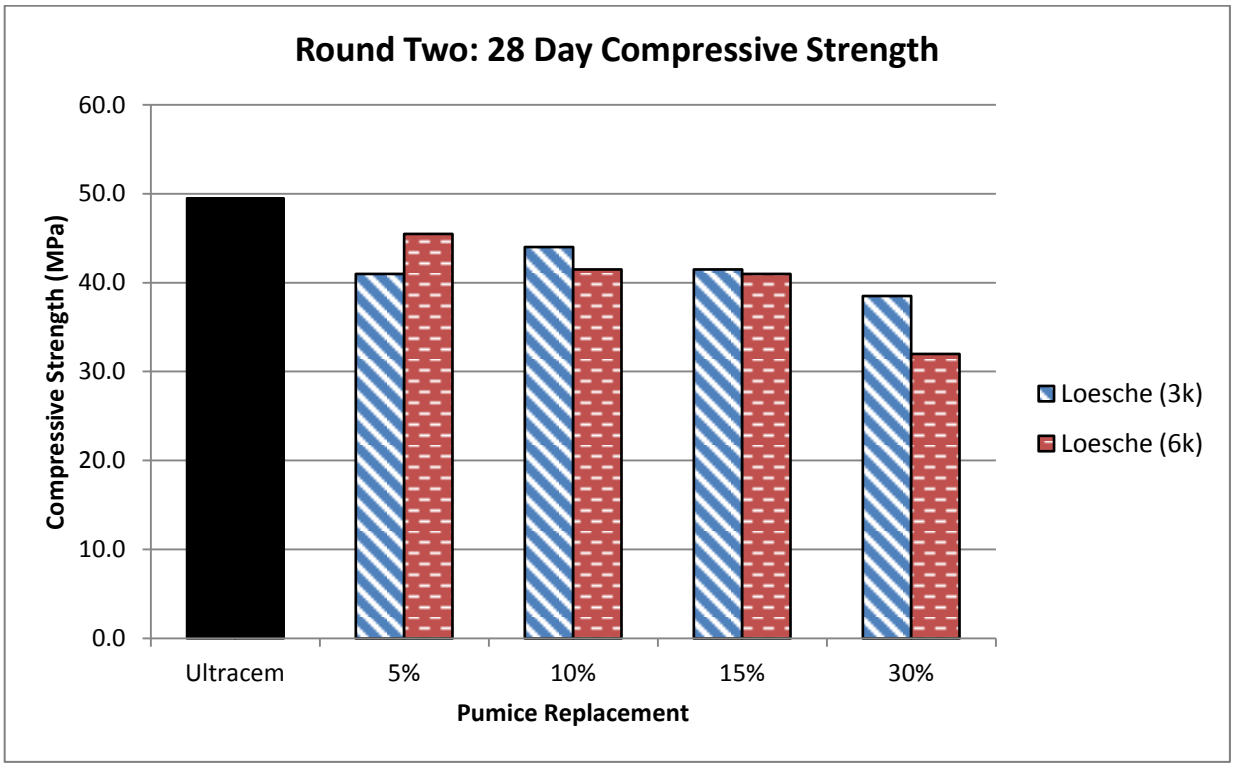

Round One: 28 Day Concrete Strength
60.0
50.0
40.0
30.0
20.0
10.0
0.0
Compressive Strength (MPa)
Ultracem
5%
10%
15%
30%
Pumice Replacement
Loesche (3k)
Loesche (6k)

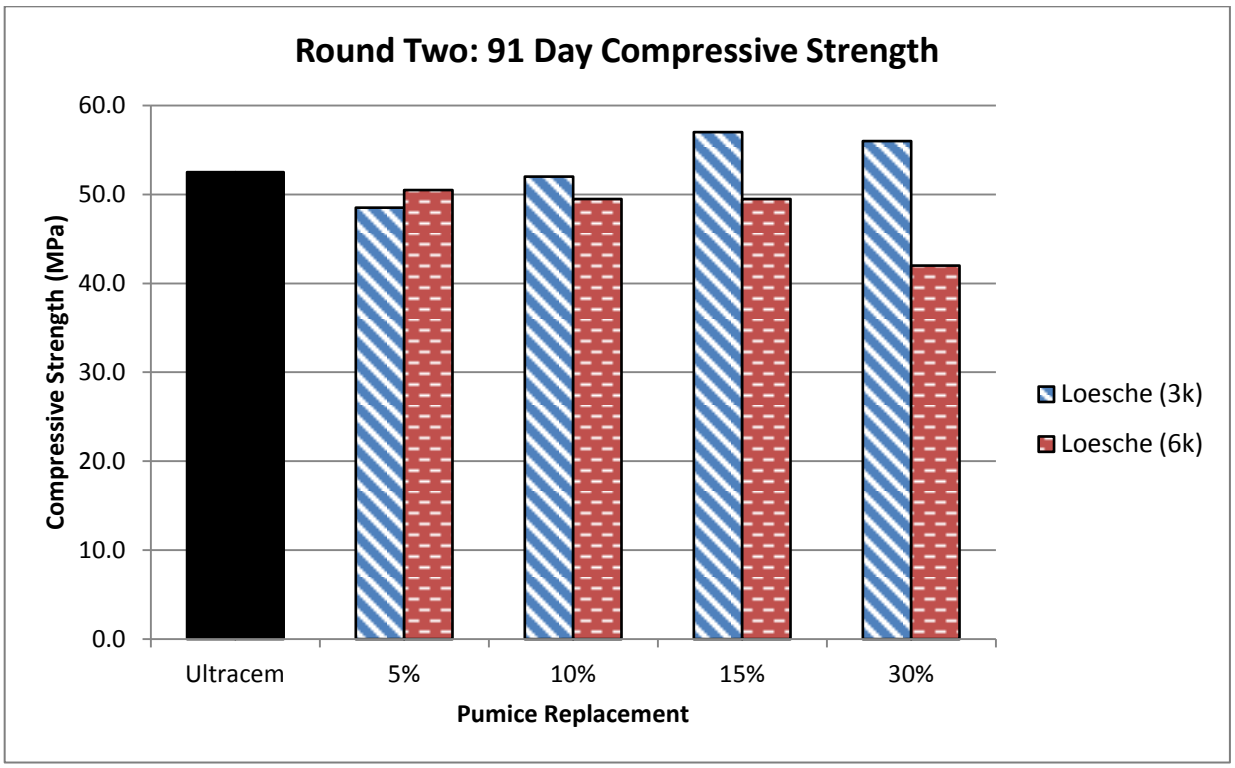

Round One: 91 Day Concrete Strength
60.0
50.0
40.0
30.0
20.0
10.0
0.0
Compressive Strength (MPa)
Ultracem
5%
10%
15%
30%
Pumice Replacement
Loesche (3k)
Loesche (6k)

Appendix 8 Round Two Concrete Strength

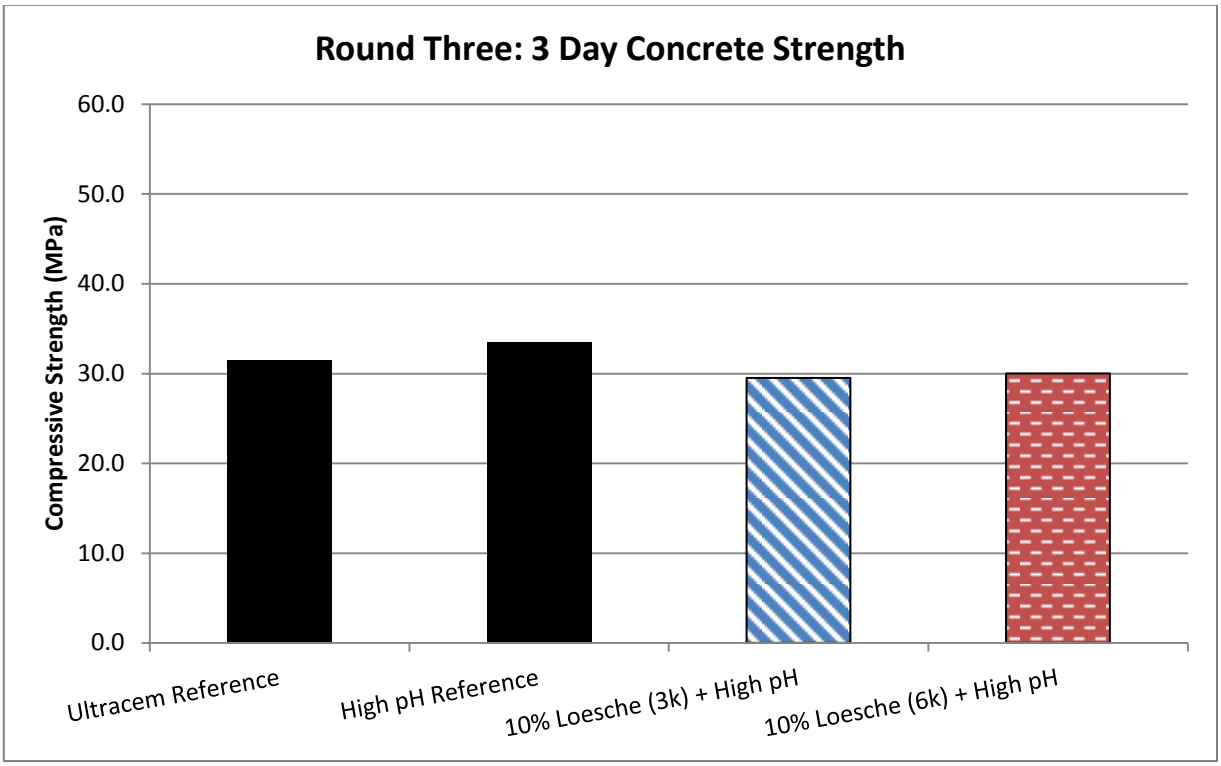


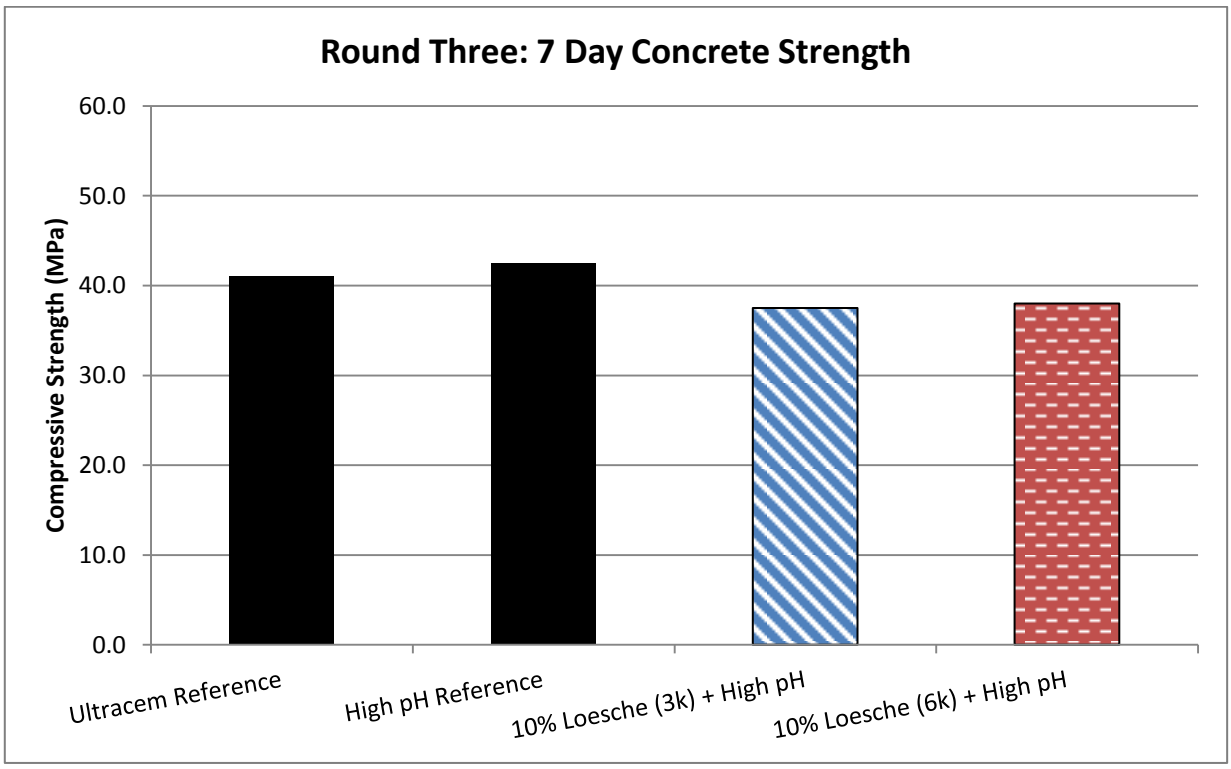


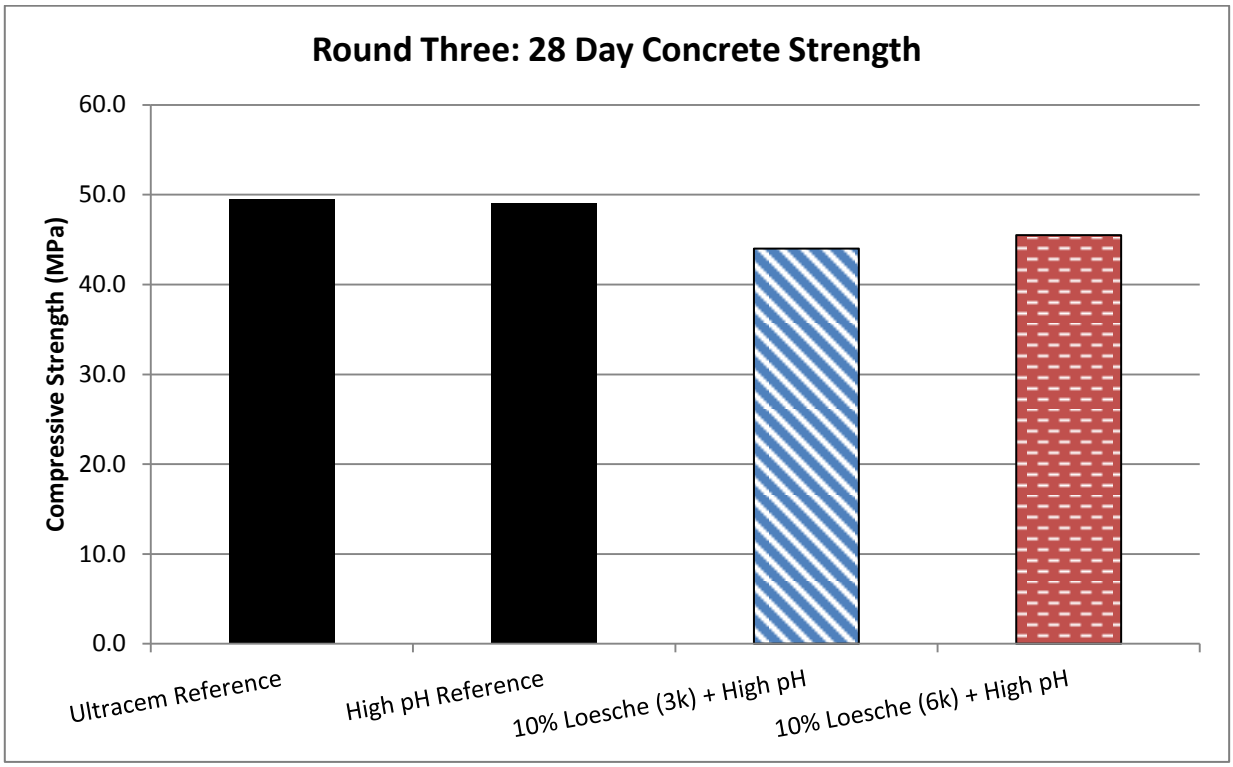

Round Two: 28 Day Compressive Strength
60.0
50.0
40.0
30.0
20.0
10.0
0.0
Compressive Strength (MPa)
Ultracem
5%
10%
15%
30%
Pumice Replacement
Loesche (3k)
Loesche (6k)

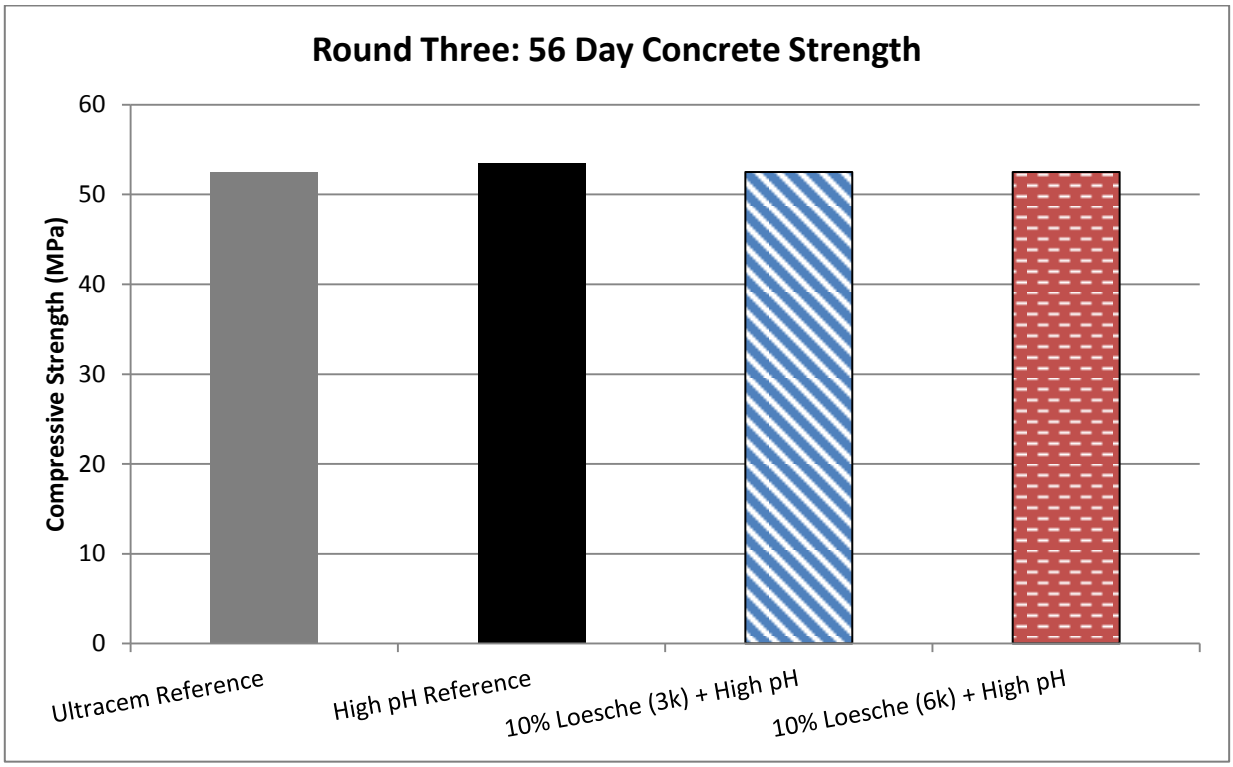

Round Two: 91 Day Compressive Strength
60.0
50.0
40.0
30.0
20.0
10.0
0.0
Compressive Strength (MPa)
Ultracem
5%
10%
15%
30%
Pumice Replacement
Loesche (3k)
Loesche (6k)

Appendix 9 Round Three Concrete Strength

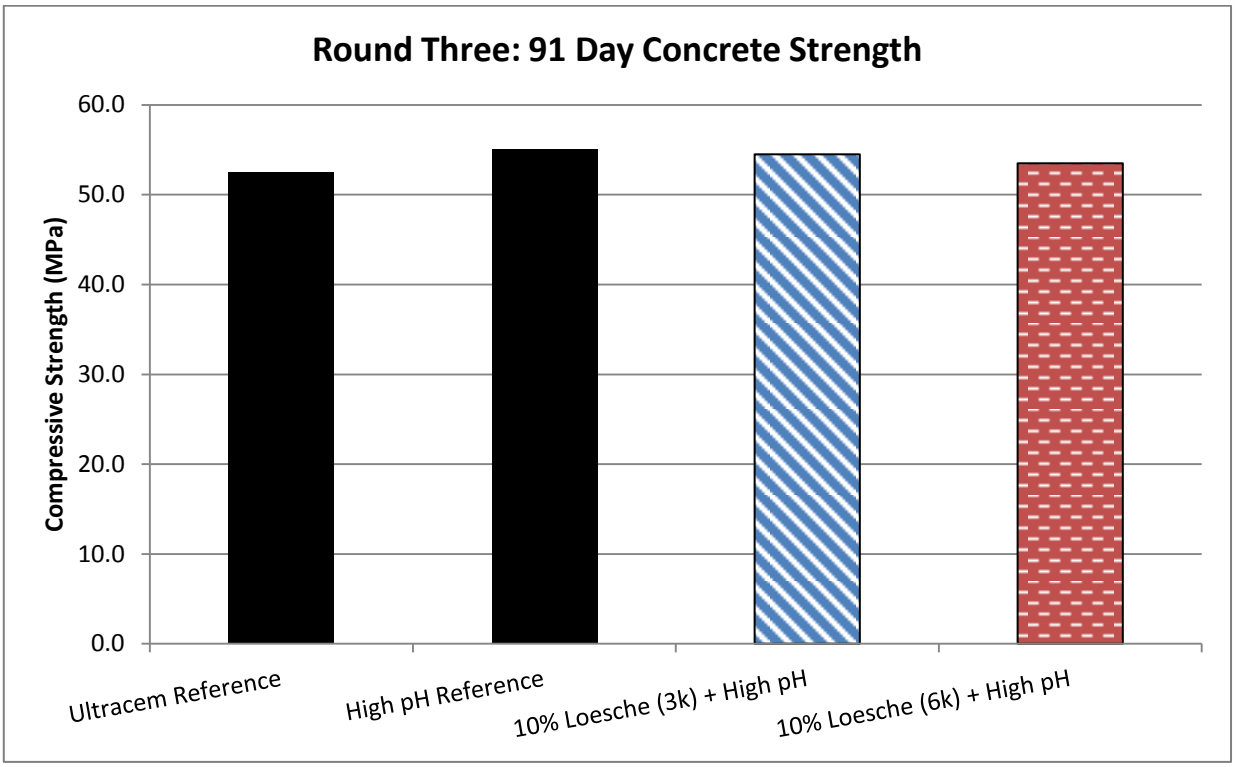




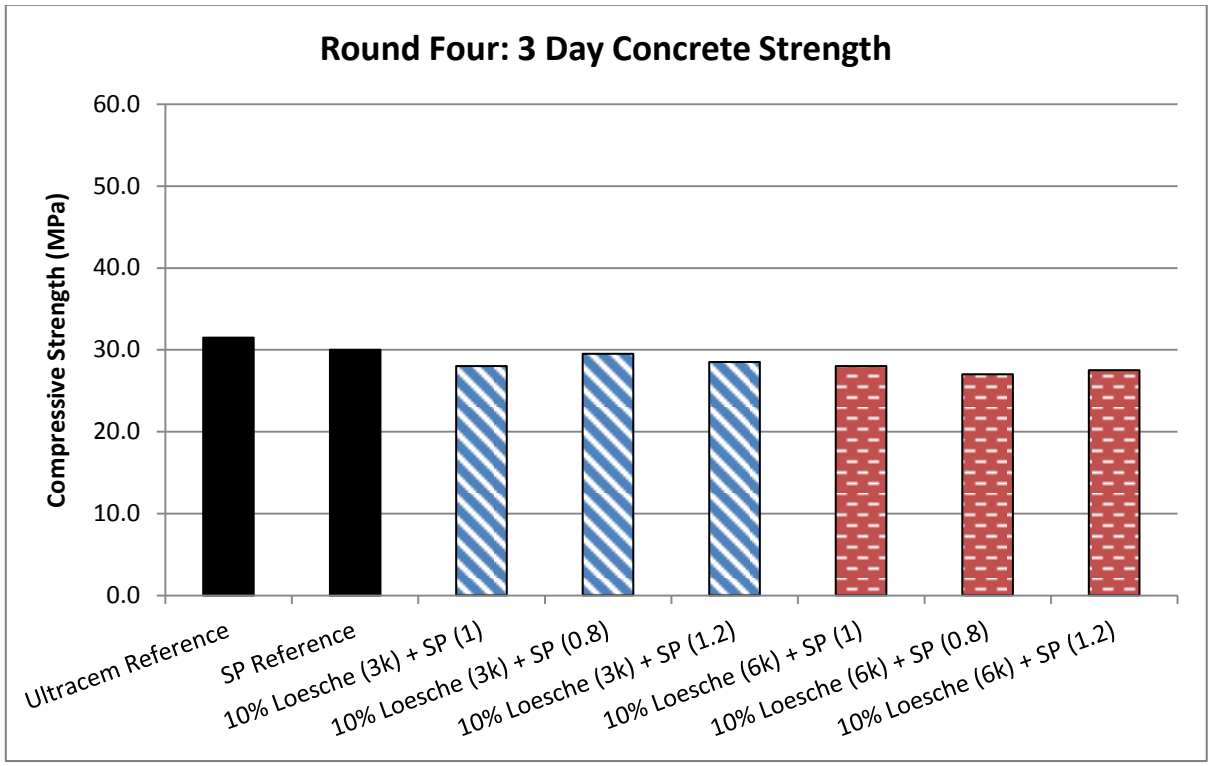


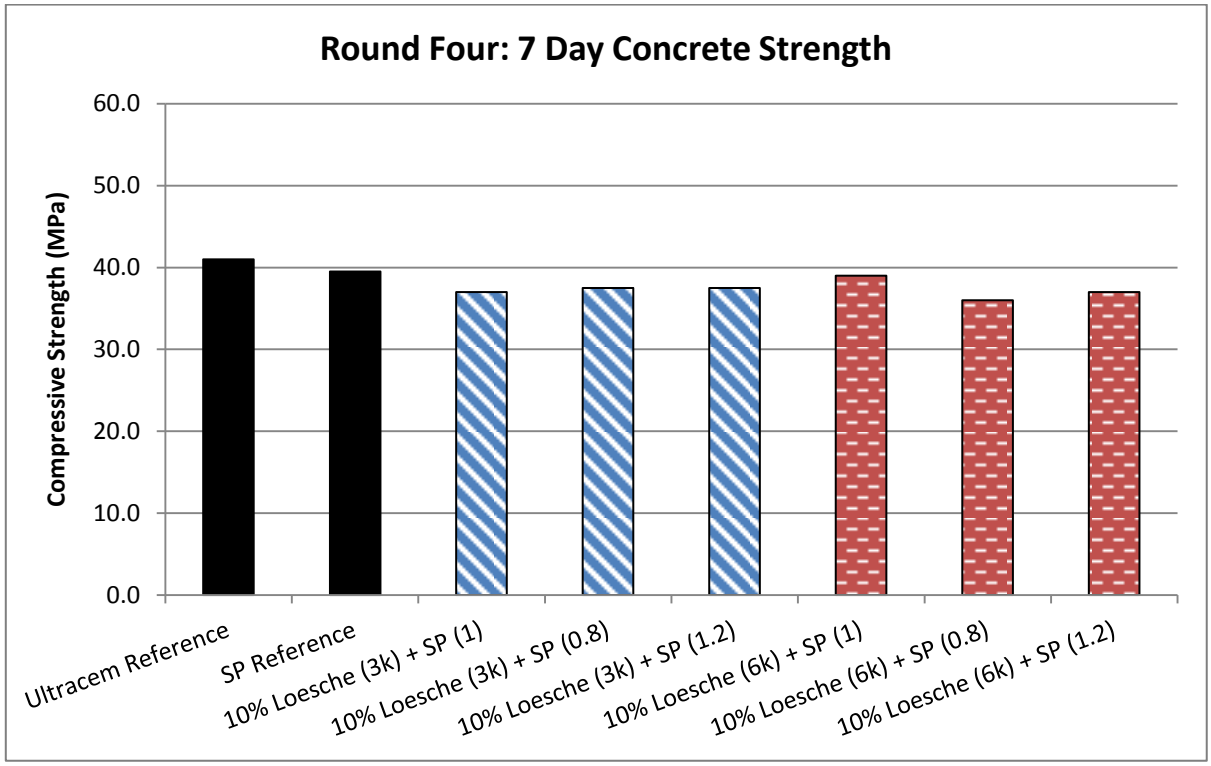


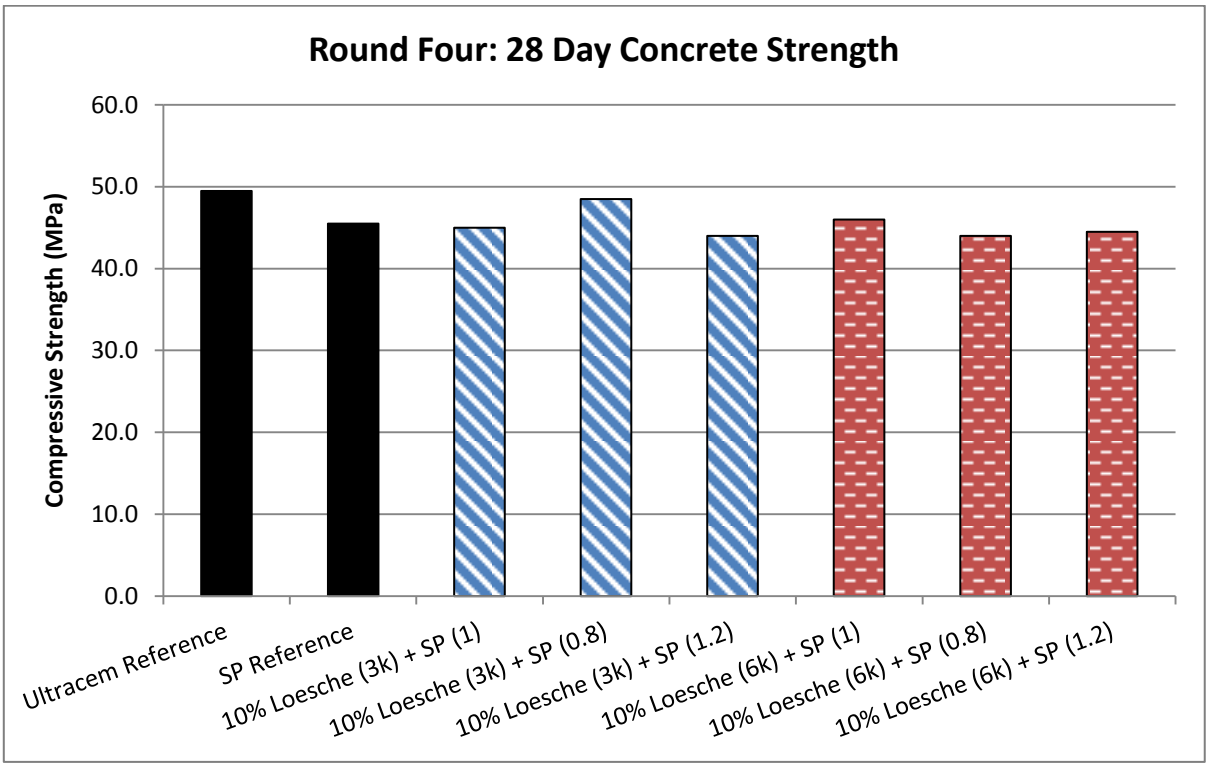
(N.B. 91 day Ultracem Reference used as a guide only)

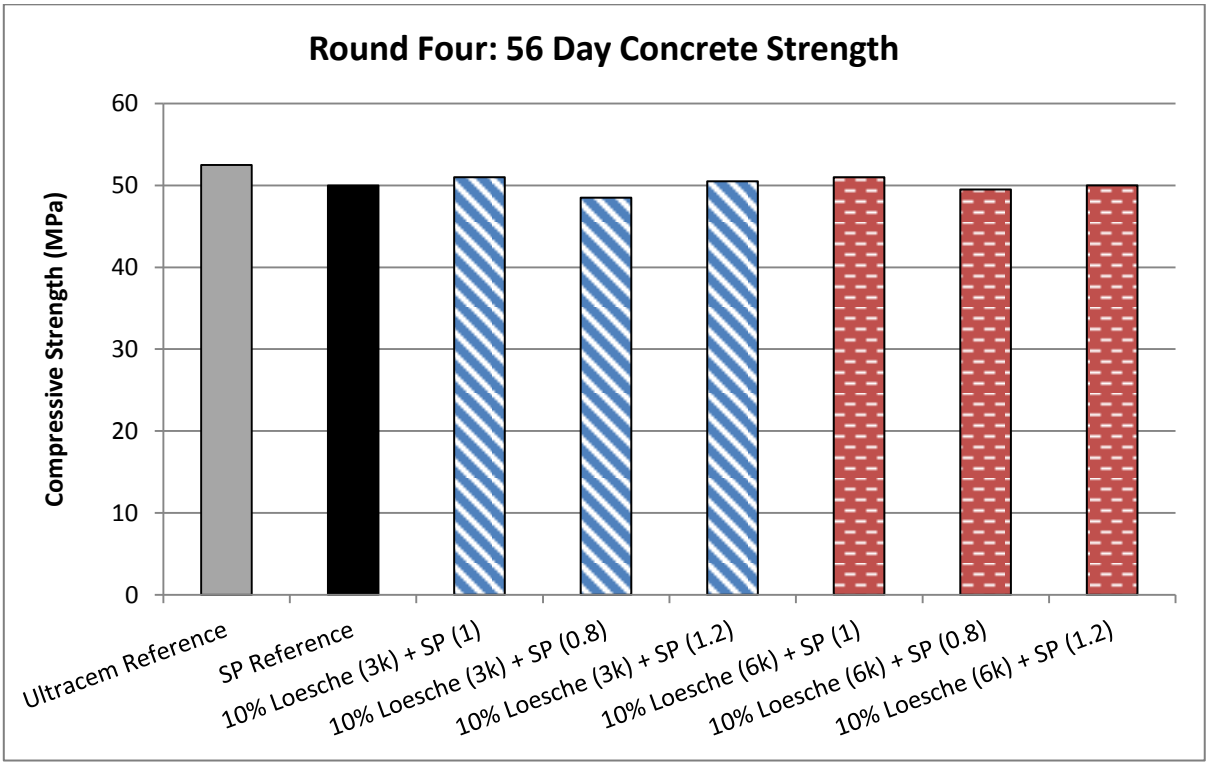

Round Three: 91 Day Concrete Strength
Compressive Strength (MPa)
60.0
50.0
40.0
30.0
20.0
10.0
0.0
Ultracem Reference
High pH Reference
10% Loesche (3k) + High pH
10% Loesche (6k) + High pH

Appendix 10 Round Four Concrete Strength

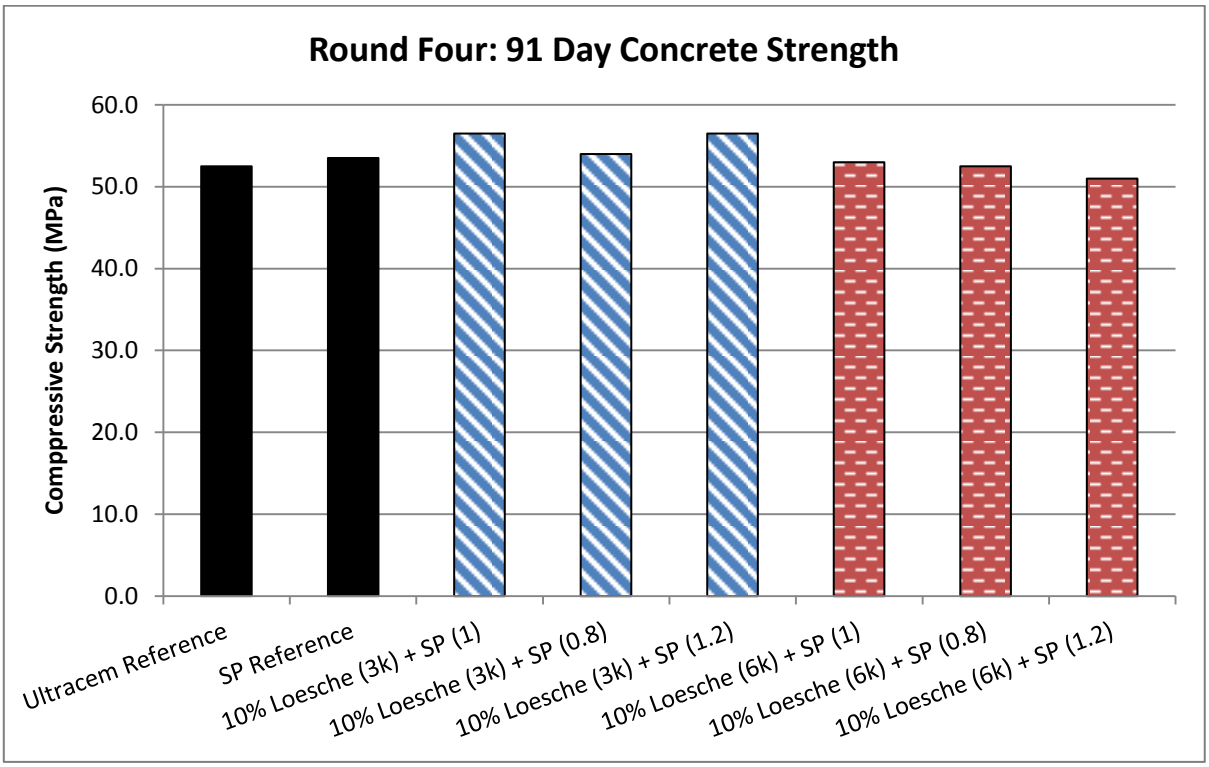




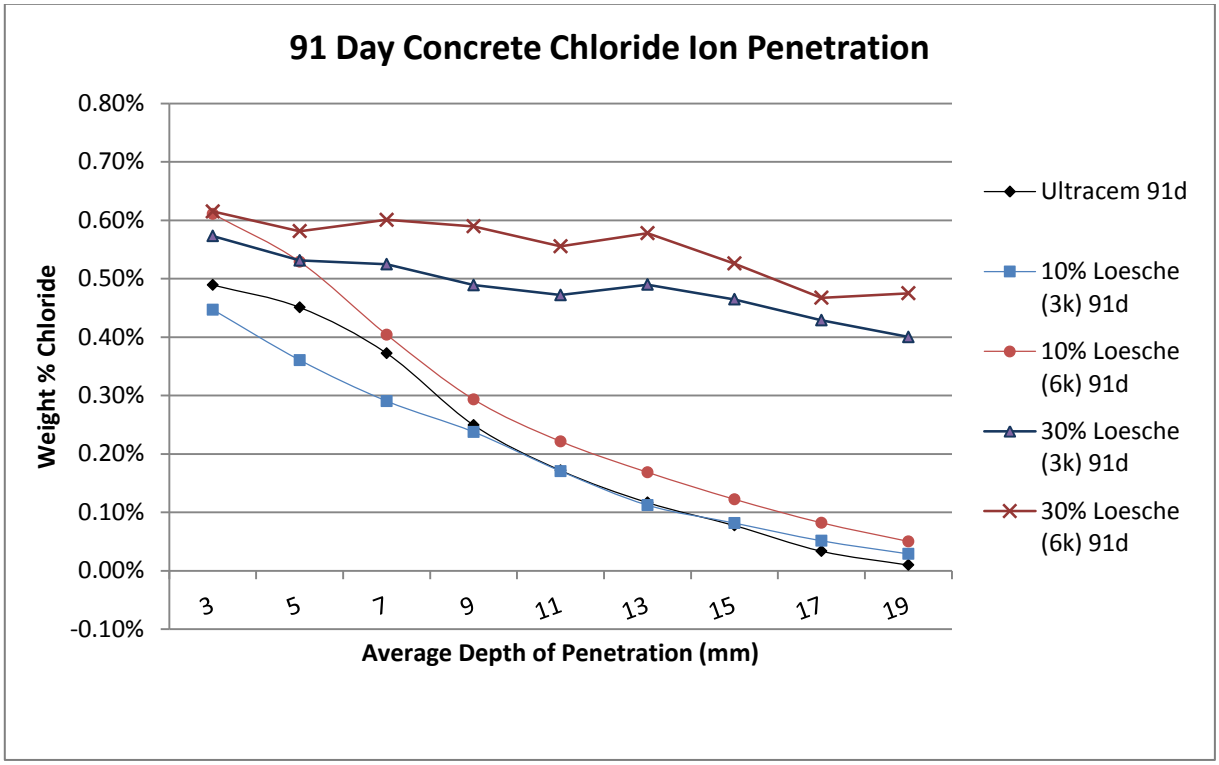




(N.B. 91 day Ultracem Reference used as a guide only)


Round Four: 91 Day Concrete Strength
Comppressive Strength (MPa)
60.0
50.0
40.0
30.0
20.0
10.0
0.0
Ultracem Reference
SP Reference
10% Loesche (3k) + SP (1)
10% Loesche (3k) + SP (0.8)
10% Loesche (3k) + SP (1.2)
10% Loesche (6k) + SP (1)
10% Loesche (6k) + SP (0.8)
10% Loesche (6k) + SP (1.2)

Appendix 11 91 Day Bulk Diffusion



N.B. 30% chloride ion penetration results are disregarded at 91 days, due to experimental error. These are provided as a reference only.